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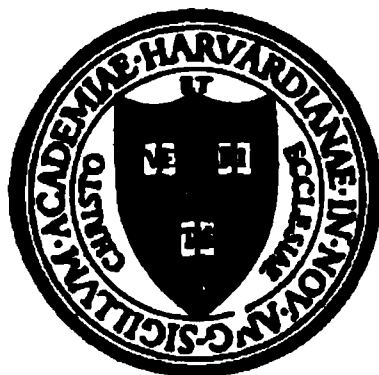
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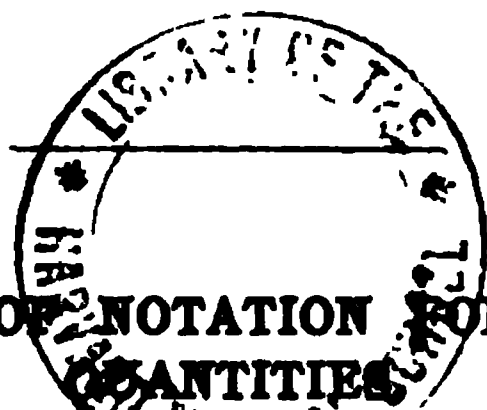
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A PROPOSED SYSTEM OF NOTATION FOR PHYSICO-CHEMICAL

QUANTITIES
BY ARTHUR L. LORAN.

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In spite of the considerable amount of attention which the matter has received, no system of notation for physico-chemical quantities has yet been devised of a character sufficiently satisfactory to secure its general adoption. The fact that the matter is to be considered by the new International Association of Chemical Societies leads the writer to present in this paper the outlines of a system of notation which has been worked out gradually through a series of years, in connection with the publications and lecture work of this laboratory. The development of the system was also greatly aided by the consideration given to the matter some years ago by a committee of representatives of various American scientific societies. It is presented here not as a final plan, but with the hope that it may be useful as a basis of further discussion.

In the writer's opinion the problem has usually been attacked on the wrong side. Instead of first formulating certain fundamental principles upon which a system might be consistently constructed, the specific task has been undertaken at once of assigning symbols to the large number of separate quantities. There is, moreover, at best, great difficulty in securing a fair compromise between the development of a rational, consistent system, and the retention of such specific symbols as are in general use. As a rule, adequate systematization seems to the writer to have been too greatly subordinated to the desire to retain familiar symbols. On the other hand, in some of the systematic plans proposed by individuals too little effort has been devoted to reconciling the notation with that in general use.

The following principles are suggested as the basis of the system of notation:

1. Quantities should be expressed by such symbols as can be conveniently used and readily distinguished, both in printing and writing. The symbols should also be such as can be described by short simple names.

2. Four distinct alphabets (styles of letters) are necessary and sufficient for a satisfactory system of notation of physico-chemical quantities.¹ If only three alphabets are employed, the same symbol has too often to be used to represent distinct quantities; or else, in order to avoid this, letters which are not in common use have to be used for many quantities.

3. The alphabets that can be best employed seem to be:

1. Italic small letters (*a, b, c*).
2. Italic capitals (*A, B, C*).
3. Black-face Roman capitals (**A, B, C**).
4. Greek letters (both small letters and capitals).

The main objection to the black-face Roman capitals seems to be that they are too prominent in comparison with the other letters. This objection is to be weighed against the advantage of the great simplicity of the Roman letters. It is especially desirable to use a style which printers are accustomed to use in ordinary composition. Other styles that might be used are ordinary Roman capitals (*A, B, C*), black-face small letters (**a, b, c**), Roman small capitals (*A, B, C*), or italic small capitals (*A, B, C*). What is essential, in the writer's opinion, is that some fourth alphabet be consistently employed for a certain group of quantities. The following expression of the Helmholtz equation illustrates the use of three of the styles in a single formula:

$$T \frac{dE}{dT} = \frac{Q}{F} - E.$$

4. The letters of any one alphabet should, in general, be used only for quantities related to certain specified divisions of science.

5. Fundamental geometrical and mechanical quantities should be represented by italic small letters; energetic, thermal and chemical quantities, by italic capitals; electrical quantities by black-face Roman capitals; optical quantities by Greek small letters; special mathematical or mechanical quantities by Greek capitals or small letters. Abbreviations of the names of mathematical functions (such as log, sin) should be represented by Roman small letters. In manuscript the style of letter is to be indicated by the usual conventional signs—italics by underlining with a straight line, black-face by underlining with a curved line. In black-board work and other similar writing, the italic small letters and capitals

¹ In physics, where magnetic quantities are also to be dealt with, a fifth alphabet would be desirable for these.

are to be represented by script letters, the black-face capitals by printed Roman letters.

6. The attempt should not be made to indicate the units in which quantities are expressed by the use of different symbols.

7. Different values of the same kind of quantity should be indicated by numerical or literal subscripts or by accents.

8. The specific value of any quantity (that is, the value of it when the other determining factors have the value unity) may be represented by overlining the symbol representing the quantity in general. Thus, if v is volume, \bar{v} is specific volume; if R is resistance, \bar{R} is specific resistance. The overline may be omitted when no misunderstanding is likely to result.

9. The same symbol is not to be used for different quantities which are likely to occur in the same expression, but may be so used, if necessary, where the quantities rarely occur together (especially if none of them are very common or fundamental ones).

10. A letter that is almost universally employed in all languages to denote a certain quantity should be adopted for that quantity, but (except in case of Greek letters) it should be in the alphabet corresponding to the nature of the quantity, as defined in paragraph 5.

11. In the choice of other symbols the primary consideration should be the development of a consistent, non-conflicting system of notation. A secondary consideration should be to secure conformity with the international usage. In case following the most common usage would introduce serious complications into the system, or in the case of conflicting usage, a symbol not in common use may be employed; but in such cases a symbol suggesting the Latin form of the name of the quantity, or if this is not practicable, its Teutonic form is to be preferred.

12. In a system of notation proposed for general acceptance only those quantities should be included which are fairly fundamental in character or are of frequent occurrence.

The following table shows a system of notation developed in accordance with these principles:

SYSTEM OF NOTATION OF PHYSICO-CHEMICAL QUANTITIES.

GEOMETRICAL AND MECHANICAL QUANTITIES.

a area; acceleration; van der Waals' constant; activity. ¹	d differential; density.
b van der Waals' constant.	e base of natural logarithms.
c concentration. ²	f force.
	g acceleration by gravity.

¹ Defined by the equation $dF = RTd \log a$.

² In formula weights or moles per unit-volume unless otherwise stated. For concentration in equivalents per unit-volume, the symbol C or C is proposed.

<i>h</i> height.	<i>p</i> pressure.
<i>i</i> moles from one formula weight or the van't Hoff coefficient; ¹ square-root of minus one ($\sqrt{-1}$).	<i>q</i> —.
<i>j</i> —.	<i>r</i> radius.
<i>k</i> constant.	<i>s</i> solubility. ²
<i>l</i> length; distance.	<i>t</i> time; temperature centigrade. ³
<i>m</i> mass or weight (as quantity of matter).	<i>u</i> velocity.
<i>n</i> number (of terms, revolutions, etc.); number of molecules.	<i>v</i> volume.
<i>o</i> —.	<i>w</i> weight (as force).
	<i>x y z</i> coördinates, variables, unknowns.
	<i>x</i> mol-fraction.

ENERGETIC, THERMAL AND CHEMICAL QUANTITIES.

<i>A</i> atomic weight; work-producing power. ⁴	<i>M</i> molecular weight.
<i>B</i> constant.	<i>N</i> number of formula-weights or mols. ⁷
<i>C</i> heat capacity.	<i>O</i> —.
<i>D</i> —.	<i>P</i> power.
<i>E</i> energy in general.	<i>Q</i> heat absorbed.
<i>F</i> free energy. ⁵	<i>R</i> gas-constant.
<i>G</i> —.	<i>S</i> entropy.
<i>H</i> internal-energy function. ⁶	<i>T</i> absolute temperature.
<i>I</i> —.	<i>U</i> internal energy.
<i>J</i> mechanical equivalent of heat.	<i>V</i> —.
<i>K</i> equilibrium-constant.	<i>W</i> work.
<i>L</i> latent heat (of vaporization, solution, fusion).	<i>X Y Z</i> coördinate axes.

ELECTRICAL QUANTITIES.

<i>A</i> —.	<i>M</i> —.
<i>B</i> —.	<i>N</i> number of faradays; number of equivalents.
<i>C</i> electrical capacity; concentration in equivalents per unit volume.	<i>O</i> —.
<i>D</i> density (of charge or current).	<i>P</i> —.
<i>E</i> electromotive force.	<i>Q</i> quantity of electricity.
<i>F</i> faraday.	<i>R</i> resistance.
<i>G</i> —.	<i>S</i> —.
<i>H</i> —.	<i>T</i> transference number.
<i>I</i> current strength.	<i>U</i> mobility of ions.
<i>J</i> —.	<i>V</i> potential.
<i>K</i> dielectric constant.	<i>W</i> —.
<i>L</i> conductance.	<i>X Y Z</i> —.

¹ Defined by the equation $\Pi = icRT$.² In formula weights or moles per unit-volume unless otherwise stated.³ In cases where confusion between time and centigrade temperature might result the latter may be represented by θ or by T .⁴ Measured by the work produced when the change in question takes place reversibly.⁵ Defined by the equation $F = A + \Sigma(pv)$.⁶ Defined by the equation $H = U + \Sigma(pv)$.⁷ For "number of equivalents" the symbol \mathbb{N} or N is proposed.

OPTICAL AND SPECIAL QUANTITIES.

α angle of optical rotation; empirical coefficient.	ν refractive index.
β empirical coefficient.	ξ —.
γ degree of ionization.	ξ —.
Γ —.	π ratio of circumference to diameter.
δ variation sign, residual.	Π osmotic pressure.
∂ partial differential.	ρ refractive power.
Δ increment.	σ surface tension.
ϵ —.	Σ summation sign.
ζ —.	τ —.
η viscosity; efficiency.	u velocity of light.
θ angle.	γ —.
\odot —.	φ angle; fluidity.
i intensity of light.	\bullet —.
κ heat-capacity ratio (C_p/C_v).	$X\psi$ —.
λ wave length; mean free path.	$\bullet\overline{F}$ —.
A equivalent conductance.	ω angular velocity.
μ micron; magnetic permeability.	Ω —.

Attention may be called to two or three important inconsistencies or defects in the above system. Time and centigrade temperature are both represented by the same symbol t . This is proposed for the reason that it is desirable to represent these two fundamental, very commonly occurring quantities by simple suggestive symbols such as are in common use, and for the reason that the confusion arising from the use of the same symbol for these two quantities is not very serious, since they seldom occur together. Density and the differentiation sign are also represented by the same symbol d , which again is not very serious, since they seldom occur together. Number of equivalents N and equivalent concentration C are represented by a style of type which is otherwise used only for electrical quantities; for this there is, however, a certain logical justification, since in electrochemical considerations equivalents are often involved. These inconsistencies can be removed by representing these quantities by letters of a special style, preferably by italic or Roman small capitals, thus representing centigrade temperature by τ , density by D , number of equivalents by N , and concentration in equivalents per unit-volume by c . The writer is inclined to favor making these symbols optional.

Some additional specifications which it seems desirable to make are as follows:

1. Partial values of a quantity of any kind are to be indicated by appropriate subscripts, not by distinct symbols. For example, partial pressures by $p_1, p_2, p_{H_2}, p_{CO_2}, \dots$; partial volumes by v_1, v_2, \dots ; separate potentials by E_{Ag}, E_{Cl}, \dots ; ion mobilities and conductances by $U_{K+}, U_{Cl-}, \Lambda_{K+}, \Lambda_{Cl-}$.

2. The molal values of various quantities would be represented under the proposed system by such symbols as $M\bar{v}$, $M\bar{C}$, $M\bar{L}$. It may be desirable to introduce some sign to indicate the molal value. Overlining with a curved line or with two straight lines is suggested; for example, \bar{v} , \bar{C} , \bar{L} or \bar{v} , \bar{C} , \bar{L} .

3. Critical and reduced quantities are to be indicated by the subscripts c and R, not by special symbols; for example, T_c , T_R , v_c , v_R , p_c , p_R .

4. Ions and the sign and magnitude of their charges are to be indicated by very small plus and minus signs attached to the chemical symbols as superiors, not written in the line above it. For example, K^+ , Ba^{++} , Cl^- , SO_4^{--} .

5. In mass-action expressions concentrations may be expressed by enclosing the chemical symbols within parentheses; for example, $(H_2)(I_2) = K(HI)^2$.

6. In expressions of the properties of dilute solutions, quantities pertaining to the solvent (or zero concentration of the solute) are to be indicated by the subscript zero; quantities pertaining to the solute or solution by letters without subscripts (or by numerical subscripts 1, 2...).

The following equations illustrate the expression of a few of the more important physico-chemical relations by the above system of notation:

$$pv = NRT = \frac{1}{2}nMu^2.$$

$$n/N = \text{the "Avogadro constant."}$$

$$\frac{C_p}{C_s} = \frac{5}{3} \frac{\Delta E_K}{\Delta E}.$$

$$\frac{p_0 - p}{p_0} = \frac{N}{N + N_0} = x; \text{ or } p = p_0 \frac{N_0}{N + N_0} = x_0 p_0.$$

$$\Pi = RT \frac{d_0}{M_0} \log \frac{p_0}{p}.$$

$$L = I/R = I/E; L = \bar{L}a/l.$$

$$E_M = \bar{E}_M - \frac{RT}{NF} \log C_{M+}.$$

$$M\rho = \frac{M}{d} \frac{v^2 - 1}{v^2 + 2}; v = \frac{\sin \varphi_1}{\sin \varphi_2} = \frac{v_1}{v_2}.$$

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BOSTON, December, 1911.

Fig. 1.

FRACTIONAL CRYSTALLIZATION OF THE PICRATES OF THE RARE EARTHS.

BY L. M. DENNIS AND C. W. BENNETT.

Received November 3, 1911.

Earlier work in this laboratory having shown that the picrates of the rare earths may easily be prepared, and that they crystallize readily from aqueous solutions, the investigation described below was undertaken to ascertain whether these salts could be utilized to advantage in the separation of the rare earths. If the results had shown that the method gives the usual gradual separation of the earths that is characteristic of most methods of fractional crystallization, the process would scarcely have merited description, for advances in this field are chiefly to be looked for in methods that will accelerate the separation of the earths. The picrates of the rare earths appear to facilitate the rapid concentration of certain groups of earths, and for this reason the details of the method and the results that it yielded are here briefly described.

Material.—In this first trial of the method it was thought advisable to use mixtures of earths containing members of the yttrium, erbium and didymium groups. Consequently a residue that was in hand and that contained chiefly earths of the didymium group was mixed with the earths obtained from xenotime. Both portions of the material contained cerium and thorium, which were removed by chlorination and treatment with a 10% solution of hydrogen dioxide. The earths were then precipitated from slightly acid solution with oxalic acid. The oxalates were washed with boiling water on a Büchner filter, were dried, and were then ignited in quartz trays about 32 cm. long, 15 cm. wide and 3 cm. deep, which were heated in a muffle furnace. The total weight of the oxides thus obtained was about 1500 grams.

Since the oxides of the rare earths do not dissolve readily in picric acid, they were converted into the hydroxides by solution in hydrochloric acid and precipitation with ammonium hydroxide. Before precipitation as the hydroxides a portion of the solution was treated with hydrogen sulfide, but no precipitate resulted. The rare earth hydroxides were repeatedly washed by decantation with water. After the last washing the supernatant liquid was siphoned off, and a hot solution of picric acid was poured upon the moist hydroxides. The material was actively stirred by a blast of air, and in this manner solution of the hydroxides was rapidly effected. The addition of the solution of picric acid was continued until most of the hydroxides had been dissolved and until the solution, after thorough stirring, failed to turn Congo-red paper blue. The solution was then separated from the residual hydroxides by filtration, and the residue was again treated with picric acid, the filtrate from this treatment being added to the main portion. There was

finally obtained a residue of reddish brown color that was insoluble in picric acid, and that was found to consist chiefly of ceric hydroxide. This point is of interest in that it shows that rare earth material which has been freed from cerium so completely as to show no trace of that element when tested with hydrogen dioxide will disclose further amounts of cerium upon treatment of the hydroxides with picric acid.

Fractional Crystallization of the Picrates.—The neutral solution of the picrates of the rare earths, obtained as above described, was then subjected to fractional crystallization in enameled iron pans holding from 20 to 25 liters each. Six of these pans were used in the beginning, but as soon as the fractions were sufficiently reduced in size, the crystallization was continued in large porcelain evaporators. Two hundred and sixty-three fractional crystallizations were made, which yielded, following the usual method of uniting the crystals on the one hand and the mother liquors on the other, a series of 25 final fractions.

The absorption spectra of the final fractions were plotted, and the atomic weights of these fractions were determined by precipitating the earths as oxalates and ascertaining the $R_2O_3 : 3 C_2O_3$ ratio.

In the examination of the absorption spectra of the fractions, the picrates were precipitated with oxalic acid, the oxalates were thoroughly

18
14
13
12
11
10

washed with boiling water, dried, and ignited to the oxide. These oxides were then dissolved in hydrochloric acid to solutions of uniform strength containing 20% R_2O_3 . A Krüss spectroscope was used, and this was calibrated against the Fraunhofer lines of the sun spectrum and the spectrum of the mercury lamp. The thickness of the chloride solution was 47 mm. The absorption bands were plotted in the usual manner on the basis of their width and intensity. It was further attempted, however, to obtain an approximate idea of the concentration of each solution in respect to those earths that give absorption bands by measuring the *relative* intensities of the bands in successive fractions. To permit of the accomplishment of this object the arrangement of apparatus shown in Fig. 1 was devised. Three cells, containing three separate fractions to be compared, were placed in front of the slit on a grooved wooden block that could easily be moved to the left and right across the field. To the ends of this block was attached a cord that could be drawn to the right or left by rotating with the fingers of the right hand the small cylinder shown in the figure. The source of light was an oxy-hydrogen flame impinging on a disk of zirconium oxide.

The results of the fractionation are shown in Figs. 2 and 3. Fig. 2 gives the changes in the atomic weights in the final 25 fractions, while

Fig. 3.

Fig. 3 shows the changes, as the fractionation proceeded, in the intensities of certain specified bands of those earths that yield absorption spectra.

Examination of these curves shows that with an original material of an atomic weight of 116 containing earths of the yttrium, erbium and didymium groups fractional crystallization of the picrates from aqueous solution yields the following results:

(1) A concentration of praseodymium and neodymium in the first fractions followed by rapid decrease of these two elements after the sixth fraction.

(2) A peculiar increase in the amounts of praseodymium and neodymium in the tenth and nineteenth fractions.

(3) A sudden concentration of erbium and holmium in the eighth fraction, and an entire absence of these two elements in the first six fractions of the series. To ascertain whether there was any detectable amount of erbium in the sixth fraction, the 20% solution of the chlorides used for the examination of the absorption spectrum was evaporated to a thick syrup and its spectrum reexamined. Even under this conditions no erbium bands were visible.

The fractional crystallization of the picrates of the rare earths appears to furnish excellent means of effecting a rapid concentration of praseodymium and neodymium practically free from erbium and holmium, and concentration of erbium and holmium with but relatively small amount of the members of the didymium group. The peculiar rise in the concentration of praseodymium and neodymium in the tenth and nineteenth fractions is under further investigation.

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THE SOLUBILITY OF IODINE IN AQUEOUS SOLUTIONS OF BROMIDES OF POTASSIUM AND SODIUM.

BY JAMES M. BELL AND MELVILLE L. BUCKLEY.

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The great increase in the solubility of iodine in water due to the presence of iodides and of bromine due to the presence of bromides has been attributed to the formation in solution of polyiodides and polybromides.¹ Some of these polyhalides have been isolated. The compound KI_3 has been described by Johnson,² but its existence at 25° has been questioned by Abegg and Hamburger;³ this same compound has been described also by Wells, Wheeler and Penfield,⁴ who have also recorded the follow-

¹ This same phenomenon has been called by Parsons, "Solution in a dissolved solid" (*J. Physic. Chem.*, 11, 659 (1907)).

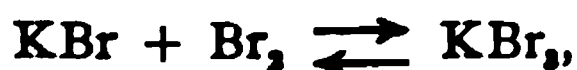
² *J. Chem. Soc.*, 31, 247 (1877).

³ *Z. anorg. Chem.*, 50, 403 (1906).

⁴ Wells and Penfield, *Am. J. Sci.*, [3] 43, 17 (1892); Wells, Wheeler and Penfield, *Ibid.*, [3] 43, 475 (1892); 44, 42 (1892).

ing compounds of the same type together with analyses, crystallographic data and methods of formation: CsI_3 , CsBr_3 , RbI_3 , RbBr_3 ; and also the higher polyhalides: CsI_4 and CsBr_4 . Still higher bromides and iodides have been isolated. Abegg and Hamburger¹ obtained KI_7 from benzene solutions containing potassium iodide and iodine.

Besides the above direct evidence of the existence of polyhalides, certain physical properties of solutions containing a salt of a halogen and the free halogen indicate that some union of these has taken place. LeBlanc and Noyes² found that the freezing point of a normal solution of potassium iodide was slightly raised by the addition of iodine to the solution, and the conductance of this salt solution was diminished by the presence of pure iodine. In a recent paper by Joseph and Jinendradasa³ it is shown that bromides lighten the color of aqueous bromine solutions, the diminution of color depending on the amount of bromide added. Making the assumption that the principal action causing the color change is the formation of a tribromide,



and applying the law of mass-action to this reversible reaction, these authors obtained a satisfactory constant. In all probability, therefore, the correct assumption was made as to the nature of the reaction. Jakovkin⁴ had previously made the same assumption in the case of the iodides, namely, that the reaction may be expressed thus:



Here the quantity of uncombined iodine was determined by distribution experiments, the liquids being carbon disulfide and water in which the iodide was dissolved. The results of Dawson and Goodson⁵ indicate that iodine and sodium iodide unite when dissolved in nitrobenzene; for, the solution saturated with respect to both contains over ten times as much iodine as the solution saturated with iodine alone, and over ten times as much sodium iodide as the solution saturated with sodium iodide alone.

Thus, there are both direct and indirect evidences that some sort of union takes place between a halogen and its salt in aqueous solution.

There have also been recorded by Wells, Wheeler and Penfield⁶ the following compounds between a halogen and the salt of another halogen: CsBrI_2 , CsBr_2I , CsClBrI , CsCl_2I , CsClBr_2 , CsCl_2Br , RbBr_2I , RbClBrI ,

¹ *Loc. cit.*

² *Z. physik. Chem.*, 6, 401 (1890).

³ *J. Chem. Soc.*, 99, 274 (1911).

⁴ *Z. physik. Chem.*, 13, 539 (1894).

⁵ *J. Chem. Soc.*, 85, 794 (1904).

⁶ Wells and Penfield, *Amer. J. Sci.*, [3] 43, 17 (1892); Wells, Wheeler and Penfield, *Ibid.*, 43, 475 (1892); 44, 42 (1892).

RbCl_2I , RbClBr_2 , RbCl_2Br , KBr_2I , KCl_2I , CsCl_2I , RbCl_4I , KCl_4I , $\text{NaCl}_4\text{I} \cdot 2\text{H}_2\text{O}$, $\text{LiCl}_4\text{I} \cdot 4\text{H}_2\text{O}$. With this direct evidence that mixed salts are also formed, it might be expected that there would also be the indirect evidence of a great increase in solubility of a halogen due to the presence in solution of a salt of another halogen; for example, that the solubility of iodine would be very greatly increased by the presence of an alkali bromide, just as the presence of one mole of potassium bromide in dilute solution causes one mole of bromine to pass into solution, and more than one mole of bromine when the solution is more concentrated.¹ Furthermore, the work of Dawson and Goodson,² using nitrobenzene as solvent and potassium bromide and iodine as solutes, seems to indicate some union of the solutes. Both of these solutes alone have relatively slight solubilities in nitrobenzene, but each influences the solubility of the other in a very remarkable way. The solution saturated with both potassium bromide and iodine contains 2.52 moles I_2 and 0.71 moles potassium bromide per liter. Regarding the possibility of the formation of compounds, the authors say: "The two series of solutions approximate in composition as the concentration increases, and the identity of the two final solutions indicates that saturation with regard to both components has now been reached. The composition of the solution saturated with iodine makes it appear probable that the complex perhalogen compounds present in solution are of the same type as those in solutions of the alkali iodides, although the evidence in support of this view is not nearly so decisive."

The present work was undertaken to determine whether double compounds of iodine with sodium or potassium bromide were indicated by a possible large increase in solubility of the halogen due to the presence of the bromide in aqueous solution. The method of procedure was similar to that of Worley,³ who determined the quantity of bromine dissolved in various potassium bromide solutions.

To aqueous solutions of sodium and potassium bromides, iodine was added in excess, and the bottles were rotated in a thermostat at 25° , electrically heated and controlled. Equilibrium was shown to be established when titrations for free iodine gave the same results as on one or two days previously. The following table and figure give these results.

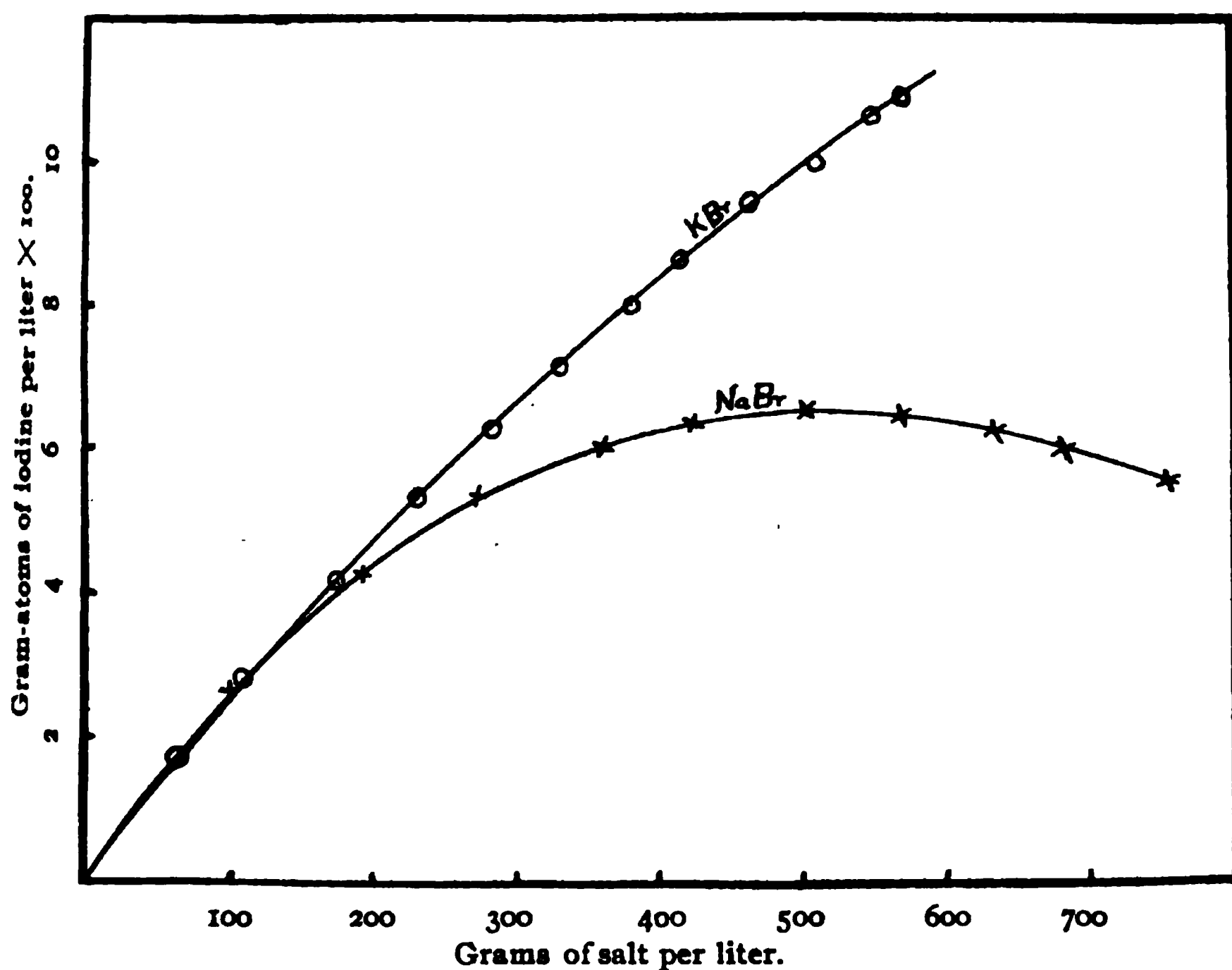
Each curve is concave downwards, indicating that each successive addition of the salt causes the solubility of iodine to increase by smaller and smaller amounts. These curves are unlike the curve of Worley³ for the solubility of bromine in potassium bromide solutions, where

¹ Worley, *J. Chem. Soc.*, 87, 1107 (1905).

² *J. Chem. Soc.*, 85, 796 (1904).

³ *Loc. cit.*

NaBr per liter Grams.	Iodine per liter. Gram-atoms.	KBr per liter. Grams.	Iodine per liter. Gram-atoms.
96.4	0.0266	60.6	0.0176
187.7	0.0425	106.9	0.0278
271.8	0.0538	175.9	0.0415
357.4	0.0598	229.8	0.0532
422.4	0.0638	281.9	0.0628
499.1	0.0648	330.6	0.0717
569.9	0.0644	377.1	0.0797
632.0	0.0622	411.0	0.0864
679.7	0.0595	461.7	0.0948
750.5	0.0551	509.8	0.1006
756.1 (sat'd)	0.0550	548.0	0.1062
		567.9 (sat'd)	0.1094



each successive addition of the salt causes the solubility of bromine to increase by greater and greater amounts. Not only are these cases different from that of Worley in kind but also in degree. For each mole of bromide in solution there was at least one mole of bromine in excess of that dissolved by the water alone. In the present cases the increase in solubility of iodine is of the order 10^{-2} mole iodine for each mole of salt. Moreover, in concentrated solutions of potassium bromide the ratio is somewhat less than 10^{-2} and in concentrated solutions of sodium bromide the ratio is considerably less than 10^{-2} . Consequently it follows from these solu-

bility measurements, that if compounds of iodine and a bromide exist at all in aqueous solution, they are present in very minute quantities.

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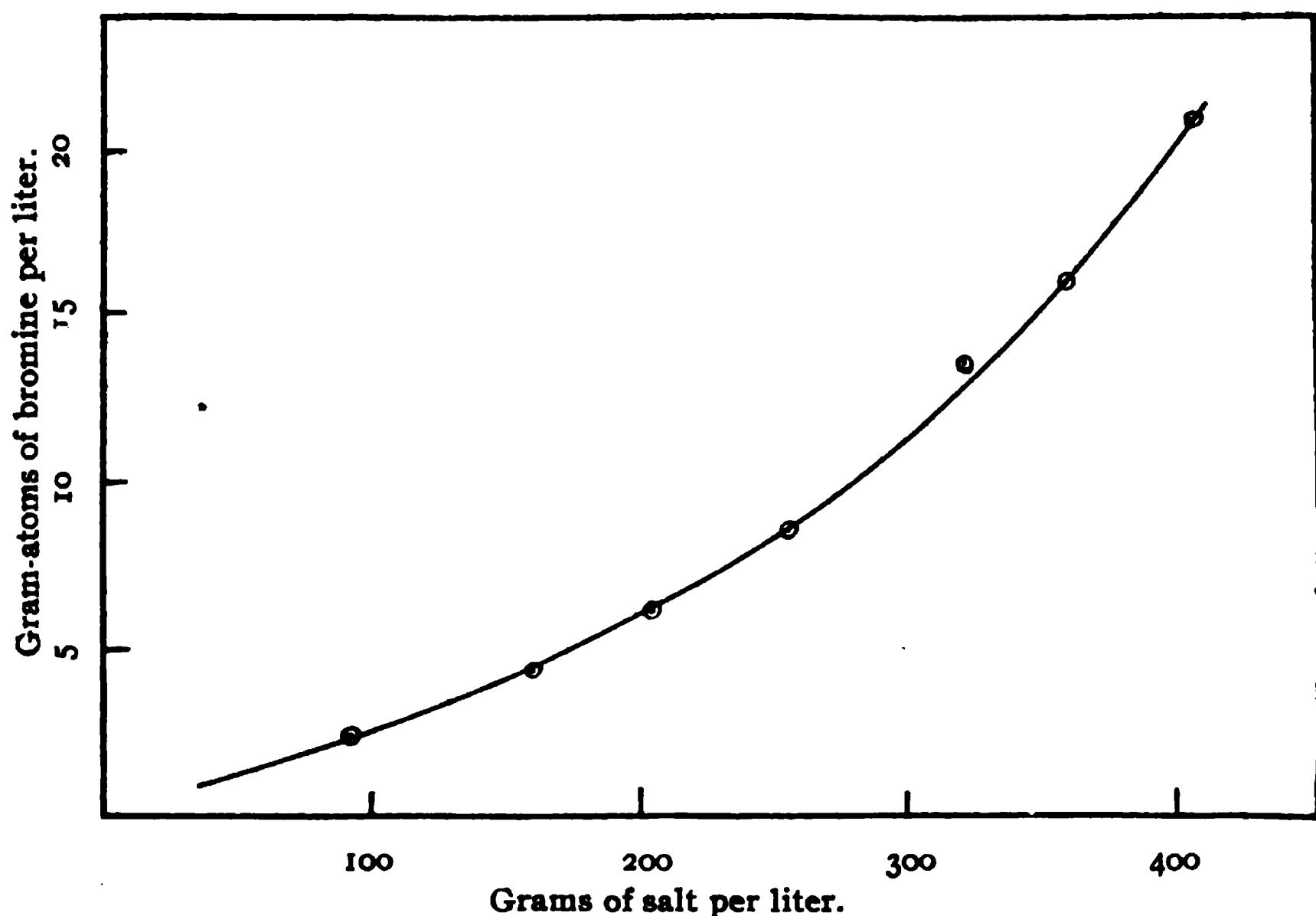
THE SOLUBILITY OF BROMINE IN AQUEOUS SOLUTIONS OF SODIUM BROMIDE.

BY JAMES M. BELL AND MELVILLE L. BUCKLEY.

Received October 26, 1911.

Reference was made in the preceding paper to the results of Worley on the solubility of bromine in solutions of potassium bromide and of Joseph and Jinendradasa on the color changes in bromine solutions due to the addition of bromides. The following table and figure give the results of solubility determinations of bromine in solutions of sodium bromide at 25°. The free bromine was estimated by adding a known volume of the solution to an excess of an iodide solution. The iodine liberated was

NaBr per liter. Grams.	Bromine per liter. Gram-atoms.	Density.
92.6	2.479	1.213
160.5	4.345	1.372
205.8	6.195	1.515
255.8	8.575	1.678
319.7	13.65	1.997
359.0	16.04	2.137
...	19.23	2.327
408.3	20.85	2.420



determined by titration against a known thiosulfate solution. The bromide in solution was determined by evaporating 10 cc. of the solution and weighing the residue.

The concentrations vary over almost the whole range up to saturation, and although the results of Worley for potassium bromide have not such a wide range, yet the two curves are similar. In dilute solutions the ratio of bromine to bromide is about 1 mole Br_2 to 1 mole NaBr but for more concentrated solutions the ratio becomes greater. For solutions of sodium bromide near saturation the ratio is about 2.5 moles bromine to 1 mole salt. For iodine¹ the ratio becomes smaller, as the concentration increases; in other words, the solubility curves for bromine and iodine in bromide solutions have opposite curvatures.

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ACTION OF AMMONIA UPON AMMONIUM THIOCYANATE.²

BY W. P. BRADLEY AND W. B. ALEXANDER.

Received November 3, 1911.

Deliquescence.—The number of substances which deliquesce in dry ammonia gas is very limited. Those which deliquesce in ammonia at ordinary temperature and at a pressure of approximately one atmosphere are the following:

Salts: NH_4SCN , ammonium thiocyanate,³ NH_4NO_3 , ammonium nitrate,⁴ $\text{Hg}(\text{CN})_2$, mercuric cyanide,⁵ $\text{Ag}_2\text{Pt}(\text{SCN})_6$, silver platini-thiocyanate.⁶

Non-metallic compounds: ICN , cyanogen iodide,⁷ BrCN , cyanogen bromide,⁸ $\text{SO}_2(\text{NH}_2)_2$, sulfamide,⁹ BI_3 , boron iodide,¹⁰ AsI_3 , arsenious iodide.¹¹

Elements: Lithium,¹² potassium,¹³ caesium,¹⁴ strontium,¹⁴ iodine.¹⁵

¹ See preceding paper.

² Read before the Conn. Valley Section, Am. Chem. Society, Oct. 7, 1911.

³ We have been unable to find any mention of this case of ammonia deliquescence in the chemical literature. The fact is known, however, in some quarters at least, among those interested in ammonia refrigeration.

⁴ Divers, *Chemical News*, 27, 37 (1873); *Z. physik. Chem.*, 26, 430 (1898). Raoult, *Compt. rend.*, 76, 1261-2 (1873). Franklin and Kraus, *THIS JOURNAL*, 27, 213 (1905).

⁵ Franklin and Kraus, *Am. Chem. J.*, 23, 300 (1900).

⁶ Peters, *Ber.*, 41, 3185 (1908).

⁷ Bineau, *Ann. chim. phys.*, 67, 234 (1838).

⁸ Bineau, *Ibid.*, 70, 257-61 (1839).

⁹ Franklin and Stafford, *Am. Chem. J.*, 28, 95 (1902).

¹⁰ Besson, *Compt. rend.*, 114, 542-4 (1892).

¹¹ Besson, *Ibid.*, 110, 1258-61 (1890).

¹² Moissan, *Ibid.*, 127, 687 (1898); *Bull. soc. chim.*, [3] 21, 906 (1899). Ruff and Geisel, *Ber.*, 39, 828-843 (1906). Kraus, *THIS JOURNAL*, 30, 657 (1908).

¹³ Ruff and Geisel, *loc. cit.* Moissan, *loc. cit.*

¹⁴ Ruff and Geisel, *loc. cit.*

¹⁵ Hugot, *Compt. rend.*, 130, 505 (1900). Colin, *Ann. chim. phys.*, 91, 263 (1814).

Compounds of carbon mono-potassium cyanacetamide¹(?), nitroform ammonia.²

This list of only sixteen substances deliquescent in ammonia at a pressure of one atmosphere and at temperatures above zero would be increased a little if substances deliquescent at temperatures below zero were to be included. Thus, potassium platino-thiocyanate, $K_2Pt(SCN)_4$, deliquesces below -10° , and the corresponding silver salt, $Ag_2Pt(SCN)_4$, below -20° (Peters); rubidium, below -3° (Ruff and Geisel); and sodium³ and barium⁴ below -20° .

Scarcely any quantitative data appear to exist for pressures higher than one atmosphere.

The meagerness of the list is due of course in part to the fact that ammonia deliquescence has not been studied as thoroughly as deliquescence in water vapor. It is far from likely, however, that ammonia deliquescence will prove to be of as frequent occurrence as the other. A substance deliquesces when the actual pressure of the vapor in contact with it exceeds the vapor tension which is characteristic of its saturated solution at the same temperature. And it must be remembered that in the case of deliquescence in water vapor we are dealing, as a rule, with a very small *partial pressure* of water vapor mixed with air, while, in every case in the foregoing list, the ammonia gas which caused the deliquescence was pure, or nearly so, and exerted therefore a pressure of about one atmosphere. We have found no recorded cases of deliquescence in ammonia under diminished pressure. It may be considered quite certain that under any considerable diminution of pressure the list would be much smaller than it is, and it is quite possible that for pressures corresponding to those of water vapor in air it might be wiped out altogether.

Of all the substances for which we have quantitative data, ammonium sulfocyanate appears to be the most deliquescent in ammonia. We have found that deliquescence ceases only at 88° . The substance which stands nearest to it in this regard is lithium, whose upper limit is 70° (Ruff and Geisel, Moissan). Caesium and strontium cease to deliquesce at 40° (Ruff and Geisel), and ammonium nitrate at 29° (Raoult), or 23° (Divers).

Compounds of Ammonia and Ammonium Thiocyanate.—It is a matter of common knowledge that ammonia unites in definit proportions with a multitude of substances, yielding so-called ammoniates, and that in many of these the ammonia plays a similar role to that of water of crys-

¹ Franklin and Stafford, *loc. cit.*

² Franklin and Kraus, *THIS JOURNAL*, 27, 214 (1905).

³ Moissan, *loc. cit.* Ruff and Geisel, *loc. cit.* Seely, *Chem. News*, 23, 169–70 (1871). Weyl, *Poggendorff's Ann.*, 121, 601–12 (1864).

⁴ Mentrel, *Bull. soc. chim.*, [3] 29, 496 (1903); *Compt. rend.*, 135, 740–2 (1902).

tallization in hydrates. Frequently one and the same substance will give two or more such compounds with ammonia. In the majority of cases more or less satisfactory analyses for these compounds are at hand. In cases where analysis is difficult, or where a set of ammoniates of a given substance is to be scouted in a preliminary way, the methods of physical chemistry afford valuable means not only of detecting their existence, but also of determining their ammonia content, as well as certain of their physical constants. In the work which follows, the solidification curve of ammonia solutions of ammonium thiocyanate is used for this purpose. The method has already been applied for the same purpose to solutions of ammonium nitrate and of water in ammonia, and has shown the existence of the compound $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$ ¹ in the one case, and of the two hydrates $\text{H}_2\text{O} \cdot \text{NH}_3$ and $\text{H}_2\text{O} \cdot 2\text{NH}_3$ ² in the other.

Experimental.

Melting Point.—The ammonium thiocyanate used was from Kahlbaum. It was purified by several crystallizations from water,³ ground and kept over concentrated sulfuric acid. The melting point of this substance is variously given in the literature, ranging from 147° to 159° .⁴ In a score or more of determinations made at various stages in our work, with salt taken both from water and from ammonia solutions, it melted constantly and sharply at 148° . The melting point was always determined in capillary tubes.

Absorptive Capacity for Ammonia.—The ammonia gas was obtained from pure concentrated ammonium hydroxide. It was dried over fused caustic potash, and by washing with its own liquid at its normal boiling point.

In two preliminary trials, made at approximately room temperature, ammonium thiocyanate absorbed 44.78% and 45.26% respectively of its own weight of ammonia. In each case the gas was passed into the salt till the weight of the latter showed no further increase. These proportions are almost exactly molecular, corresponding to 2.02 and 2.001 mols. of ammonia respectively. The product was an oily liquid, of specific gravity 0.981.

To determine whether a compound had actually been formed, or whether the molecular proportions were simply the result of an accidental choice of temperature, the absorptive power of the salt was tested at several

¹ Kuriloff, *Z. physik. Chem.*, 25, 908–10 (1898).

² Rupert, *THIS JOURNAL*, 32, 748–9 (1910).

³ Waddell has shown that the transformation of ammonium thiocyanate into thiourea practically does not occur in aqueous solutions, even when they are boiled for many hours. *J. Physic. Chem.*, 2, 527 (1898).

⁴ 159° , Reynolds, *Ann.*, 150, 227 (1869). 148° – 9° , Reynolds and Werner, *J. Chem. Soc.*, 83, 2 (1903). 149° , Findlay, *Ibid.*, 83, 407 (1904). 147° , Inghlieri, *Chem. Zentr.*, 1909, II, 905.

temperatures from 0° to 100° . At 0° the product was found to contain 43.10% of ammonia, at 25° 31.16%, at 50° 19.40% and at 75° 6.17%, while at 100° no ammonia was absorbed.

In Fig. 1 the circular plots represent direct absorption of ammonia, while the crosses represent values obtained by first saturating the salt at a lower temperature and then holding the product at the required temperature in a stream of ammonia gas till it no longer lost weight. It will be seen that the end result was sensibly the same by either method.

The percentages corresponding to molecular proportions are indicated on the axis of concentration.

Prolongation of the rectilinear upon which all of the plots lie cuts

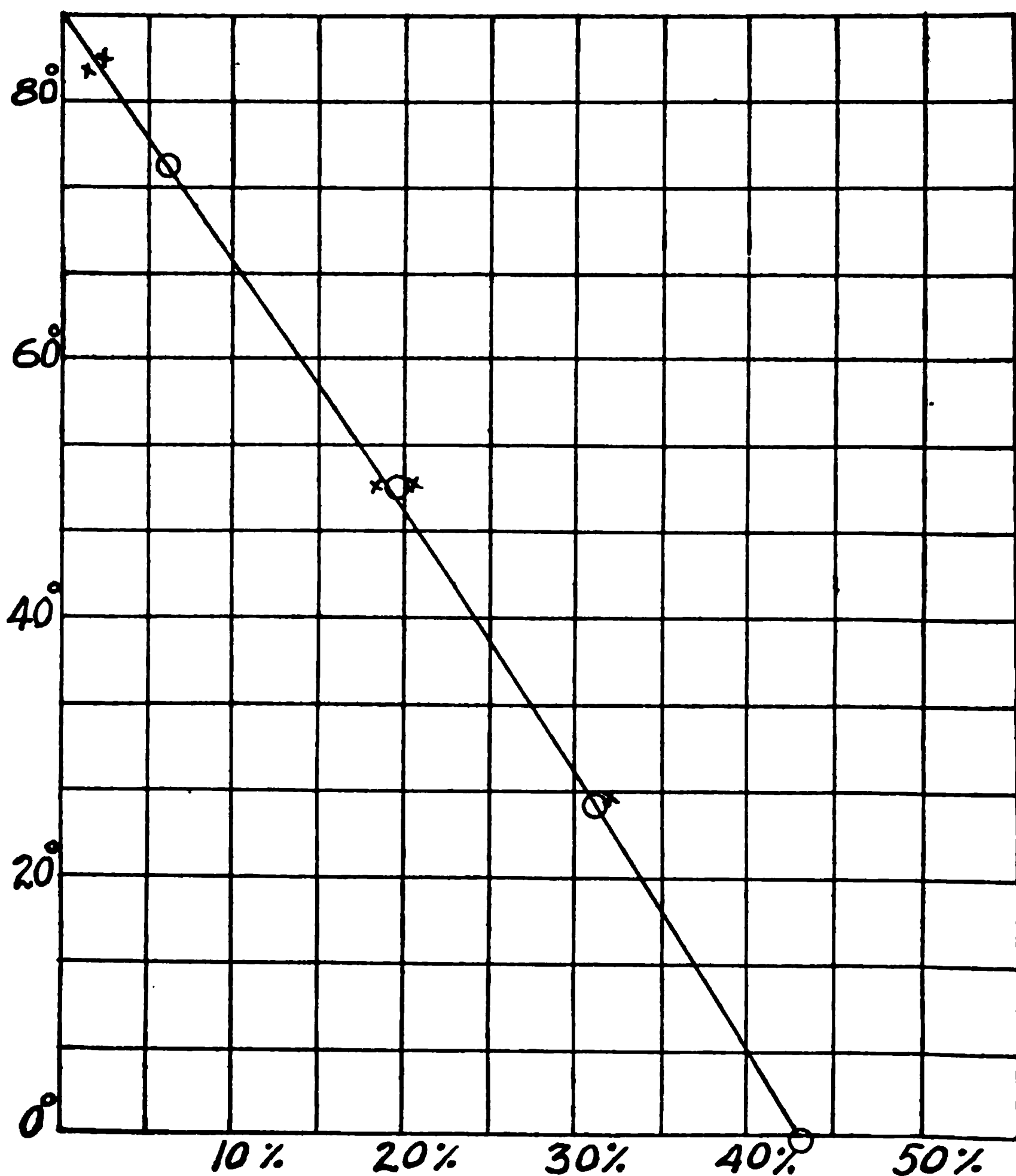


Fig. 1. Absorption curve.

the axis of temperature at 88° , which is thus the temperature at which ammonia ceases to be absorbed by ammonium sulfocyanate.

There is no basis in this curve for assuming the existence of compounds of ammonia and ammonium sulfocyanate at temperatures above zero.

Freezing-Point Curve.—Very different results were obtained at low temperatures by the study of the freezing points of solutions of ammonium thiocyanate in ammonia ranging in concentration from 0% to 100% of the latter.

The apparatus for this purpose consisted of a long-necked glass bulb about 10 cc. capacity, provided with a steel cap as shown in Fig. 2.

A is a sleeve of such diameter as just to allow the slightly belled mouth of the neck to pass. B is a similar but smaller sleeve, split in halves in the direction of its length, fitting the glass neck as tightly as possible, and screwing into A above. Hard wax was melted into the free space between the top of B and the mouth of the neck, and the latter was held meantime in such a position as to project from A by an amount equal to about half the thickness of the glass. The wax, just before setting, was kept at the right height under the bell by screwing B up or down, as might be necessary.

C is a cap provided within with a gasket of fiber or stiff rubber. It is perforated by a vent of small diameter and its gasket is likewise perforated. The vent in turn is closed by the little cap D, with its gasket. When C is screwed home, its gasket presses chiefly or wholly upon the glass.

In operation, the cap C was removed to charge the bulb with powdered salt and with ammonia. The latter was conducted to the bottom of the

bulb by means of a narrow glass tube, the bulb meanwhile being held in the vapor of liquid air, at such a height above the liquid that the ammonia would condense as fast as it was delivered, but without freezing. The weight of the tube empty, the weight when charged with salt, and again when charged with both salt and ammonia, were the data for calculating the concentration of the solution.

The solution was then cooled to its freezing point by immersing the bulb in a bath containing about equal volumes of alcohol and ether. The increasing viscosity of alcohol, if used alone at the lower temperatures, would have interfered decidedly with the maintenance of a uniform temperature. The alcohol-ether mixture, contained in a deep cylin-



Fig. 2.

drical Dewar bulb, as shown in Fig. 3, was brought first, by means of liquid air, to a temperature slightly lower than the freezing point of the solution. The bulb having been inserted, a small portion of its contents froze, and melted again very slowly indeed as the bath warmed. During the latter process, both the solution and the bath were very effectively stirred by simply spinning the bulb by hand from above, the lower end of the bulb being kept centered the while, if necessary,

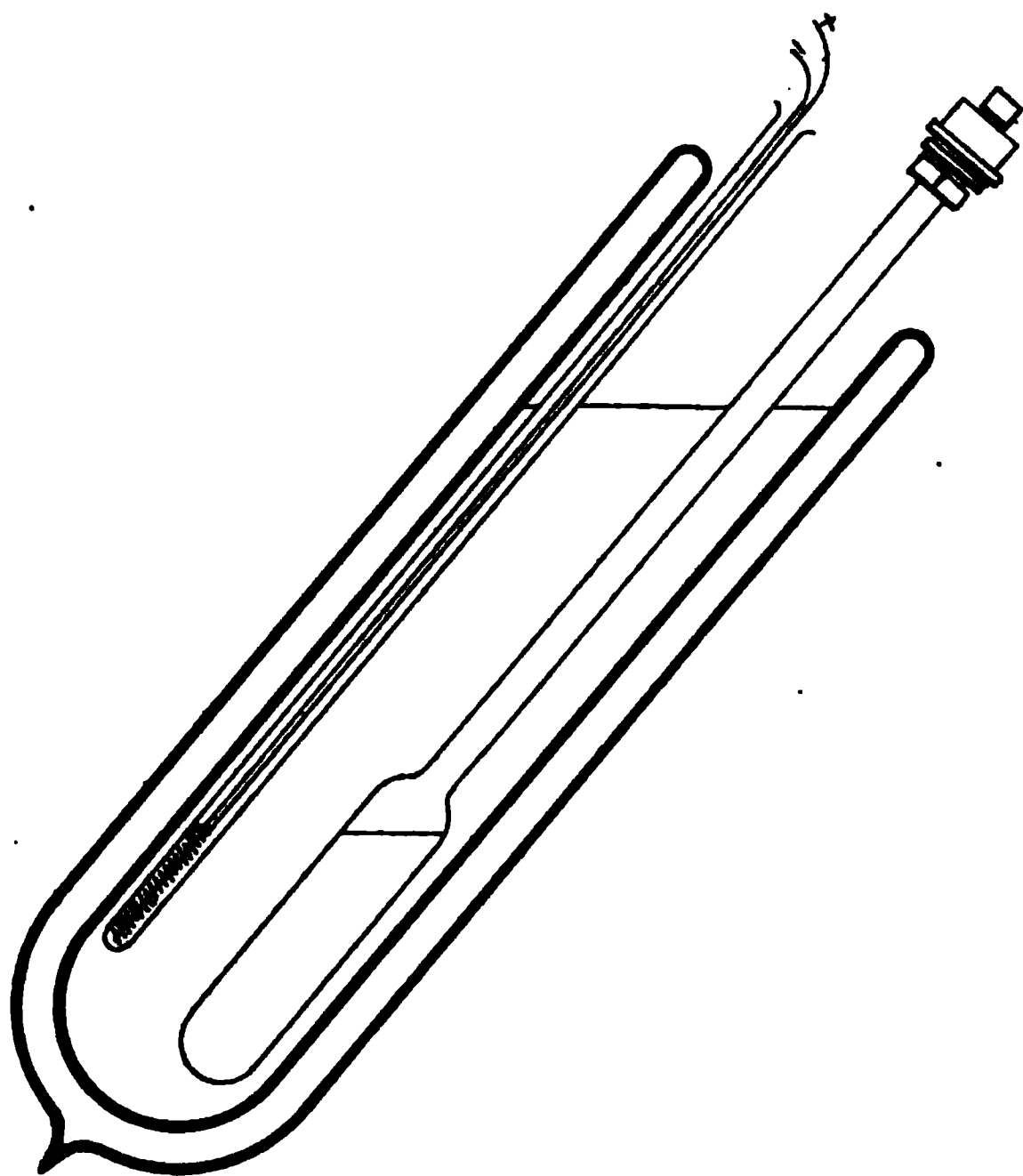


Fig. 3. Freezing-point apparatus.

by means of a simple arrangement of wire not shown. With the same object of thorough stirring in view, it was found advantageous to incline the Dewar bulb at an angle of about 45° . Just as the last crystals disappeared, the temperature of the bath was taken. Immediately after, liquid air was introduced into the well stirred bath, a few drops at a time, and the temperature was noted again just as the first crystals reappeared. If the interval between the disappear-

ance and the reappearance of crystals was brief, there was no evidence of supercooling in the solution.

Temperatures were read by means of a platinum resistance thermometer which had been thoroughly tried out in previous work, and which was standardized again for this immediate purpose by means of broken ice and a carbon dioxide-ether mixture (temperature 78.34°C).¹ This thermometer, protected by a thin-walled glass tube, was immersed several inches deep in the bath.

The arrangement of the thermometer, just described, suggests the likelihood of considerable lag in temperature, and this lag would have been realized no doubt if the temperature of the bath had been allowed to change too rapidly in either direction. By a not too cumbersome

¹ Holborn, *Ann. Phys.*, [4] 6, 245 (1901).

combination of thorough stirring, and deft manipulation of the liquid air, it was found in practice that the difference between the melting and freezing points could be reduced to a fraction of a degree. That the thermometer moreover was practically unaffected by heat conducted in through the leads is shown by the fact that the freezing point of pure ammonia was found at 76.2° . Not less than three readings were taken of each freezing point of the solution for each concentration.

Having finished with one concentration, the tube was removed from the bath, carefully dried, and weighed again at room temperature as a check. The small cap D was then opened slightly, and a very small amount of ammonia was blown off, thus giving a new concentration. A considerable number of successive determinations could thus be made with a single initial charge, until the contents of the bulb were about half gone. At this point it was found desirable to begin with a new charge of suitably greater concentration than the first, for if the bulb was much less than half full, it became somewhat difficult to detect with sufficient precision the first appearance of crystals, or the exact moment of their disappearance.

For temperatures above that of the room, a bath of warm water was substituted for the alcohol-ether, and water warmer than the bath, for the liquid air.

Results.—The following table gives the data obtained and Fig. 4 shows the course of the curve.

TABLE OF FREEZING POINTS.

% NH_3	F. p.	% NH_3	F. p.	% NH_3	F. p.	% NH_3	F. p.
0.00	148	32.29	—39.8	56.18	—79.8	66.79	—95
9.89	77	34.01	—39.2	56.63	—76.8	67.30	—93
13.22	56	36.38	—38.8	57.43	—75.8	67.93	—91.8
16.55	32	38.76	—38.8	57.77	—79	68.25	—90.3
17.62	23	42.08	—41.3	58.62	—79.8	68.84	—89
19.40	10.3	44.08	—42	59.22	—79.8	69.65	—88
20.93	—0.3	45.40	—44	59.29	—79.8	71.00	—85.7
21.91	—5.8	47.33	—47.2	60.07	—79.8	73.77	—82.7
22.50	—13.8	48.76	—52.2	60.73	—84.7	76.18	—81.3
23.27	—18	49.75	—57	61.53	—86.3	78.75	—79
23.94	—20	51.08	—60.6	61.63	—84.3	79.38	—79.2
24.89	—22	52.20	—65.2	62.33	—87	83.18	—78.7
25.61	—24.3	53.96	—70.8	63.05	—87.2	86.78	—78
26.30	—25.8	54.65	—72.8	64.55	—87.3	90.01	—77
27.67	—29.8	54.90	—73	65.60	—88.3	93.50	—76.9
29.13	—34.8	55.13	—75.7	66.11	—89.3	94.78	—76.8
29.90	—39.8	55.52	—77	66.40	—90.8	94.90	—76.7
30.75	—42.8	55.91	—79.3	66.41	—91.3	100.00	—76.2

In Fig. 4, for convenience of reference, the percentages corresponding to molecular proportions are indicated on the axis of concentration.

It will be seen that the curve furnishes sufficient evidence of the existence of three compounds, at least. These are ammoniates containing three, six and eight molecules of ammonia respectively. The crests are well formed and the highest points correspond accurately enough to the theoretical molecular concentrations.

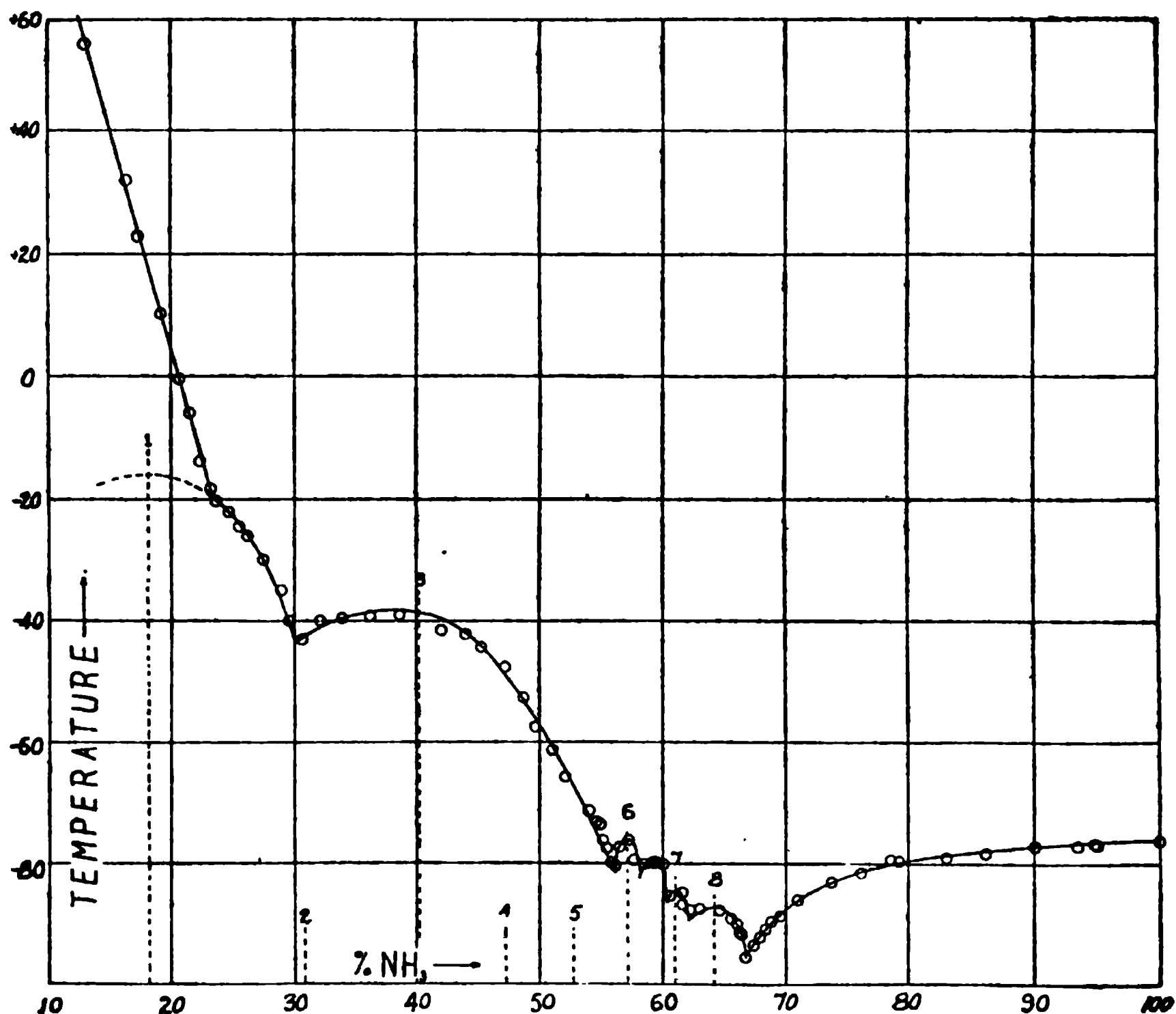


Fig. 4. Freezing-point curve.

That part of the curve which lies between 24% and 30% shows no crest. However, its prolongation would apparently culminate at about 18% ammonia, which corresponds to a mono-ammoniate. Provisionally, it will probably be safe to assume the existence of this compound, but if so, it forms only in the presence of a certain excess of ammonia. Cases of this sort are not at all uncommon.¹ Again, between 60% and 62% of ammonia there is doubtless a convolution corresponding to a hepta-ammoniate, but the numerical data are not as conclusive as might be desired. Intervals of concentration must be made much smaller before the course of the curve at this point can be considered certain. An important reason for assuming the existence of this hepta-ammoniate

¹ E. g., Kuriloff, *Z. physik. Chem.*, 23, 677 (1897).

is found in the fact that the crystals which form at this part of the curve are different from those which form on either side of it.

Finally, between 58% and 60% the plots are wholly ambiguous. Situated as they are, however, it is impossible that they should belong either to the convolution of the hepta-ammoniate on the left of them, or to that of the octo-ammoniate on their right. Clearly, also, they are poor material out of which to construct a new convolution between these two. Nevertheless, we are convinced that such a new convolution will be found here when data of sufficient accuracy come to hand, for, as in the previous case, the crystals which form in this section are distinguishable in appearance from those which form at concentrations immediately adjacent. Such a convolution would correspond to a compound, $\text{NH}_4\text{SCN} \cdot 6\frac{1}{2}\text{NH}_3$, or $2\text{NH}_4\text{SCN} \cdot 13\text{NH}_3$ (58.9% NH_3), which would be analogous to cases which occur frequently enough in salts with water of crystallization, e. g., $\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ ($= 2\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$). It remains only to add that while thus eight sorts of crystals could be distinguished by the eye it is a much more difficult, if not impossible, task to distinguish them by description. In general, however, the four sorts observed between 56% and 67% ammonia (the region of the four narrow convolutions) appeared as flakes, while the three below 56%, including ammonium thiocyanate itself, were granular. The solid ammonia, as it formed in small quantities, may perhaps best be described as jelly-like.

Considering the great complexity of the curve as a whole, it is highly desirable that the work be repeated with all possible refinements. Owing to the change of residence of one of us,¹ we shall unfortunately not be able to do this in the immediate future. It would also be interesting to determine the vapor pressure curve with a view especially to learn whether these compounds, or any of them, exist in solution at higher temperatures.

Summary.

1. Ammonium sulfocyanate is the most deliquescent substance in ammonia so far observed. It continues to deliquesce up to 88° .
2. The freezing-point curve has been determined in a preliminary way for solutions of ammonium thiocyanate in ammonia, at concentrations ranging from 0% to 100% NH_3 .
3. The solvent forms three compounds certainly, and probably five, with the solute. The former contain respectively one, three and eight molecules of ammonia; the latter, seven and six and one-half molecules.
4. The melting points are approximately as follows: the mono-ammoniate, -16° (metastable); the tri-ammoniate, -38° ; the hexa-ammoniate, -76° ; the hepta-ammoniate, -84° ; and the octo-ammoniate,

¹ (W. B. A.)

about -87° . The ammoniate, $2\text{NH}_4\text{SCN} \cdot 13\text{HN}_3$, would probably melt in the vicinity of -80° .

5. The lowest eutectic point lies in the vicinity of -96° .

CRYOGENIC LABORATORY OF WESLEYAN UNIVERSITY,
MIDDLETOWN, CONN., Oct. 17, 1911.

A METHOD OF MEASURING ABSOLUTE VISCOSITY.

BY HAROLD P. GURNEY.

Received November 2, 1911.

The desirability of expressing the viscosity of liquids in absolute units cannot be too strongly urged. Unfortunately, most methods employed to this end are either not adapted to rapid commercial work, or are not capable of giving absolutely accurate results. The advantages that may be claimed for the following method are: (1) it can be made extremely

accurate, (2) the manipulation is simple and rapid, (3) opaque liquids can be tested, (4) the apparatus can be set up in any chemical laboratory at short notice, taking but little time to calibrate, and (5) only a very small quantity of liquid is required.

The apparatus is outlined in Fig. 1. The flask *D* is connected by a stopcock, *A*, to a vacuum pump and by rubber tubing, *C*, to a vertical glass tube, *E*, of capillary bore. A stopcock, *B*, connects with the atmosphere. A cup with vertical walls contains the liquid where viscosity is to be tested. There are three marks or etched rings around the glass tube at *F*, *G*, and *H*. In Fig. 2, the apparatus is shown with a jacket for temperatures other than room temperature.

The method of operation is simple. The cup *I* is filled with liquid until it just rises inside the capillary to the line *H*. The stopcock *A* is opened and *B* is shut until the liquid has been sucked up above the line *F*. *A* is closed and *B* opened, thereby admitting atmospheric pressure above the liquid in the capillary tube. The level of the liquid in the capillary descends with but slightly

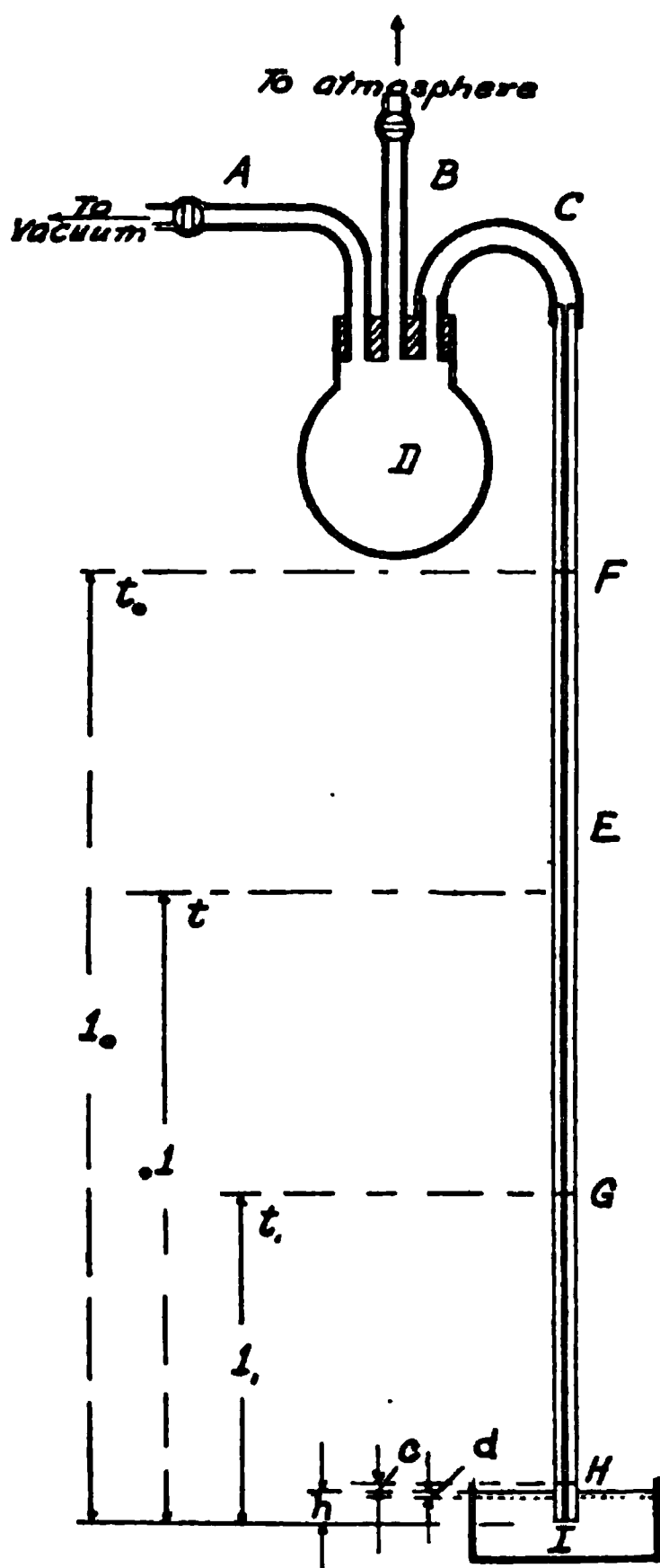


Fig. 1.

diminishing velocity, and the time required to pass from F to G is measured by stop watch. Increased accuracy may be attained by repeating and averaging results. The distances of F , G , and H from both the bottom and top of the tube are carefully measured; the density of the liquid may be obtained by any suitable method, and the radius of the capillary may be determined from the length and weight of a thread of mercury. The tube should be placed parallel to a plumb-line to insure accurate perpendicularity. In case the water or steam jacket is used, the liquid should first be sucked up, then lowered to atmospheric pressure and the liquid adjusted to H . Then it should be raised to the top of the jacket above F

*Mid
between*



Fig. 2.

until the temperature is the same as that of the jacket, waiting say a minute or two, and then allowed to descend as before. When the level of the liquid passes F , practically all of the liquid which was not exposed to the jacket will be out of the capillary. In this way, the amount of liquid to be heated up is extremely small, hence saving in time of operation.

In the following mathematical discussion, all reasonable corrections will be taken into account and some of these will later be shown to be negligible. The following notation will be employed:

- l = the distance of the level of the liquid in the capillary to the bottom of the tube at any time t .
- l_0 = the distance of F from the bottom of the tube or the level at time t_0 .
- l_1 = the distance of G from the bottom of the tube or the level at time t_1 .
- r = the radius of the capillary.
- R = the radius of the dish.
- q = the cross-section of the capillary.
- Q = the surface of the liquid in the dish.

$$\beta = q/Q.$$

h = the distance between the original surface of the liquid in the dish and the bottom of the tube.

c = the capillary head.

d = the variable depression of the surface of the liquid in the dish at time t from that of the original adjustment.

γ = the density of the liquid.

μ = the viscosity of the liquid.

g = the acceleration of gravity.

P = the pressure tending to change the velocity of the column of liquid.

a = the pressure due to the resistance of the air in the capillary tube.

v = the velocity of the capillary liquid level.

All quantities should preferably be expressed in gram-centimeter-second units. At any time t , the pressure P tending to change the velocity of the capillary column of liquid is given by the following equation:

$$P = -\frac{8\mu dl^1}{r^2 dt} + \frac{0.005 \gamma l v^2}{r} + \frac{\gamma v}{l} + c\gamma g + h\gamma g - (l + d)\gamma g + a.$$

Of these quantities $\frac{8\mu dl}{r^2 dt}$ and $l\gamma g$ are the largest, by far. Equating these alone we would obtain:

$$-\frac{8\mu dl}{r^2 dt} = l\gamma g$$

$$v = -\frac{dl}{dt} = -\frac{r^2 \gamma g}{8\mu}.$$

Since $\frac{r^2 \gamma g}{8\mu}$ is made up of constant quantities, v would be constant under this assumption. However, certain other factors cause v to vary slightly. The change in velocity of the column of liquid is small and since $P = \mu l dv/dt$ the value of P will be entirely neglected.

Also,

$$Qd = q(l - h - c),$$

$$d = \beta(l - h - c),$$

where

$$\beta = \frac{q}{Q} = \frac{\pi r^2}{\pi R^2} = \left(\frac{r}{R}\right)^2$$

and

$$\gamma g [l - h - c] [1 + \beta] - \frac{\gamma v^2}{2} - \frac{0.005 \gamma l v^2}{r} - a = -\frac{8\mu dl}{r^2 dt}.$$

Both β and the quantity $\left(\frac{\gamma v^2}{2} + \frac{0.005 \gamma l v^2}{r} + a\right)$ are small, and if $\left(h + c + \frac{v^2}{2g} + \frac{0.005 \gamma l v^2}{gr} + \frac{a}{\gamma g}\right)$ be designated by z a variable, the equation may be simplified to the form

¹ dl is itself negative since l diminishes.

$$\frac{\gamma g r^2 (1 + \beta) dt}{8\mu} = - \frac{dl}{l - z}.$$

Integrating between the limits of t_0 and t_1 , and l_0 and l_1 , respectively,

$$\frac{\gamma g r^2 (1 + \beta) (t_1 - t_0)}{8\mu} = l_0 - l_1 + z \ln \frac{l_0 - z}{l_1 - z};$$

let

$$t_1 - t_0 = T \text{ and } l_0 - l_1 = L;$$

then,

$$\mu = \frac{\gamma g r^2 T (1 + \beta)}{8 \left(L + z \ln \frac{l_0 - z}{l_1 - z} \right)}$$

and

$$z = h + c + \frac{0.005 l_m v_m^2}{g r} + \frac{v_m^2}{2g} + \frac{a}{g r}$$

where

$$v_m = L/T \text{ and } l_m = \frac{1}{2}(l_0 + l_1).$$

It will be shown later, in a numerical example, that, with all other quantities given, the value of μ may be expressed as a linear function of z instead of a complex logarithmic function; $h + c$ is the larger part of z , but for accurate work other values should be taken into account.

In regard to a/gr , the resistance head of the air in the capillary tube, this may be expressed in terms of γ_a , the density of the air; μ_a , the viscosity of the air; and l_a , the mean length of the air column in the capillary tube:

$$a = \frac{8\mu_a l_a v_m}{r^2} + \frac{0.005 \gamma_a l_a v_m^2}{r} + \frac{\gamma_a v_m^2}{2} + \frac{0.5 \gamma_a v_m^2}{2}$$

Of this expression, the three last quantities are small compared with the first, and μ_a may be expressed in terms of the absolute temperature Θ degrees centigrade by the simple relation $\mu_a = c \Theta$ where c is a constant and equal to 6.2×10^{-7} approximately,

$$\frac{a}{g r} = \frac{8c \Theta l_a v_m}{g r^2}.$$

It is directed to place the tube perpendicularly. Should, however, the tube deviate by an angle α degrees, the measured value of μ would be too large by an amount which is a fraction of its true value $\times 0.00015\alpha^2$. If the value of g is only carried to three places, it is obviously inconsistent to take into account a deviation of one or two degrees.

Let us now take up a specific numerical example. A capillary tube of one meter in length has the following dimensions: $r = 0.03475$ cm., $r^2 = 0.001207$ sq. cm., $l_0 = 78.45$ cm., $l_1 = 21.37$ cm., $l_a = 50.09$ cm., $l_m = 49.91$ cm., and $L = 57.08$ cm. Also $R = 4.4$ cm.

$$\mu = \frac{gr^2(1 + \beta)\gamma T}{8 \left(L + z \ln \frac{l_0 - z}{l_1 - z} \right)},$$

wherein

$$\beta = \left(\frac{r}{R} \right)^2 = \left(\frac{0.03475}{4.4} \right)^2 = 0.0000624.$$

The effect of β can obviously be neglected. As γ and T will differ with different liquids, we will simply endeavor to express the coefficient of γT as a linear function of z . Δ are the differences in the coefficient per unit difference in z .

z .	$\frac{gr^2}{8 \left[L + z \ln \frac{l_0 - z}{l_1 - z} \right]}$	Δ .
0.....	0.002593	0.000060
1.....	0.002533	0.000059
2.....	0.002474	0.000060
3.....	0.002414	0.000061
4.....	0.002353	0.000061
5.....	0.002292

Then within reasonable limits:

$$\frac{gr^2}{8 \left[L + \ln z \frac{l_0 - z}{l_1 - z} \right]} = 0.002593 - 0.000060 z = 0.002593(1 - 0.0231z).$$

Now,

$$z = h + c + \frac{8c\Theta l_a v_m}{g\gamma r^2} + \frac{v_m^2}{2g} \left[1 + \frac{0.005(l_1 + l_0)}{r} \right].$$

If the temperature is 20° C., $\Theta = 293.7$. Also $g = 981$; then,

$$z = h + c + 0.062 \frac{v_m}{\gamma} + 0.008 v^2.$$

When v_m is small, it can be neglected in commercial work, and if $h + c$ be made equal to 2.00 cm., then,

$$\mu = 0.00247\gamma T.$$

VISCOSITY OF SOLUTIONS OF THE METAL AMMONIA SALTS.

BY ARTHUR A. BLANCHARD AND HAROLD B. PUSHEE.

Received October 30, 1911.

In a previous article by one of the authors¹ it has been pointed out that in series of homologous liquid organic compounds, the viscosity is greater, the greater the molecular weight, and smaller, the greater the symmetry of the molecule. From this it has been assumed to be a general principle that an increase in viscosity is due to an increase in the size

¹ THIS JOURNAL, 26, 1315 (1904).

of the molecules of a liquid, or to a decrease in their symmetry, and this principle has been applied in the study of solutions of inorganic compounds. It is generally believed to-day that in aqueous solutions a weak chemical union exists between solute and solvent, and that the molecules, and particularly the ions, of the solute are not as simple as would appear from the ordinary way in which their formulas are written. It should be possible by a careful interpretation of viscosity measurements to gain considerable insight into the complexity of the molecular or ionic aggregates existing in a solution.

The method employed by us in determining viscosity was the usual one of taking the time of flow through a capillary tube. The time for the flow of a definite volume of solution under its own head, divided by the time of flow for the same volume of pure water, multiplied by the specific gravity, gives the viscosity in terms of the viscosity of water. To this value a correction has been applied, with the end in view that the viscosity value shall always be based on the same amount of water rather than on the same volume of solution. A definite bulb full of solution contains less water than the same bulb when filled with pure water. The difference is readily calculated and in applying the correction, the time of flow of this amount of water through the capillary is added to the time of flow of the solution.¹

The remarkable phenomenon of negative viscosity has been observed with a number of salts such as the nitrates, iodides, thiocyanates, etc., of potassium, ammonium, rubidium, caesium, and thallium, that is, solutions of these salts have a lower viscosity—in most cases even when the corrected viscosity is considered—than that of pure water. Addition of the salt thus decreases the internal friction of the water. According to the principle just stated, this must mean that aggregates of smaller size or greater symmetry are produced. The hydrated ions or molecules of the dissolved salt must be smaller or more symmetrical than the $(H_2O)_n$ molecules which are present in pure water.

A phenomenon similar to negative viscosity is observed when ammonia is added to solutions of copper, silver and zinc salts.² Initially a marked decrease in viscosity occurs, but after addition of two moles of ammonia for each mole of silver salt, and four moles of ammonia for each mole of copper or zinc salt, further addition of ammonia causes practically the same increase of viscosity as if it were added to pure water.

It is known that the ion complexes $[Ag.2NH_3]^+$, $[Cu.4NH_3]^{++}$, and $[Zn.4NH_3]^{++}$ exist in ammoniacal solutions. The viscosities of solutions of these ion complexes being less than of solutions of the supposedly simple metal ions Ag^+ , Cu^{++} , and Zn^{++} , it is fair to assume that the

¹ *Loc. cit.*, p. 1320.

² Blanchard, *THIS JOURNAL*, 26, 1315 (1904).

former must be smaller or more compact than the "simple" ions; and the most obvious explanation is, that the ordinary aqueous ion is a *complex* consisting of the metal ion plus bound water molecules, and that this complex is larger, or else more unsymmetrical, than the new complex formed by displacing the water molecules by ammonia molecules.

The new experimental work on this subject which has been carried out by Mr. Pushee at the Massachusetts Institute of Technology has consisted of the measurement of viscosities of solutions obtained by making successive additions of ammonia to solutions of salts of alkali and alkaline earth metals. The accompanying tables contain the experimental results.

The first column gives the concentration of ammonia in moles per liter.

The second column gives the specific gravity of the solution referred to that of water, both at the temperature of the experiment.

The third column gives the time of flow of the solution. The figure in parenthesis gives the time of flow of pure water in the same apparatus at the same temperature.

The fourth column gives the viscosity, η , as calculated in the more usual manner.

The fifth column gives the corrected viscosity, η' , in which allowance is made for the water displaced by the solute.

AMMONIA IN WATER AT 25°.

Conc. NH_3 .	Sp. gr. 25°/25°.	Time (147.8).	η .	η' .	D'.
0	1.000	147.8	1.000	1.000	...
2	0.986	155.8	1.040	1.088	0.044
4	0.973	164.2	1.081	1.175	0.044
6	0.961	172.6	1.121	1.262	0.043
8	0.946	182.8	1.169	1.316	0.050
Average,					0.044

AMMONIA IN 1.048 MOLAL NH_4Cl AT 25°.

(147.4)					
0	1.017	144.6	0.997	1.137	...
1.00	1.010	148.8	1.020	1.084	0.047
2.96	0.995	157.9	1.068	1.178	0.048
4.75	0.982	169.3	1.127	1.280	0.057
Average,					0.051

AMMONIA IN 0.548 MOLAL CaCl_2 AT 25°.

(147.8)					
0	1.047	164.8	1.168	1.180	...
1	1.040	168.9	1.190	1.225	0.045
2	1.033	173.9	1.214	1.286	0.061
6	1.008	193.5	1.325	1.478	0.048
Average,					0.050

AMMONIA IN 1.097 MOLAL Li_2SO_4 AT 25° .

Conc. NH_3	Sp. gr. $25^\circ/25^\circ$	Time (147.6).	η	η'	D'.
0.00	1.048	185.5	1.318	1.331	...
1.10	1.042	192.3	1.359	1.399	0.062
2.21	1.034	200.7	1.406	1.473	0.067
4.41	1.019	216.6	1.496	1.615	0.065
6.52	1.007	231.9	1.581	1.748	0.063
					Average, 0.064

AMMONIA IN 0.5 MOLAL LiCl AT 1° .
(285.2)

0.00	1.014	302.0	1.073	1.081	...
1.00	1.006	314.3	1.110	1.143	0.062
1.97	1.001	325.4	1.142	1.197	0.056
2.50	0.998	331.6	1.161	1.229	0.060
2.96	0.995	335.7	1.172	1.250	0.046
4.06	0.989	349.7	1.215	1.318	0.062
					Average, 0.058

AMMONIA IN 1.504 MOLAL LiCl AT 1° .
(285.2)

0.00	1.037	382.4	1.207	1.234	...
1.97	1.024	363.5	1.306	1.379	0.074
3.92	1.010	398.5	1.409	1.531	0.078
5.15	1.003	419.7	1.477	1.626	0.077
7.65	0.998	470.9	1.663	1.839	0.085
					Average, 0.076

The sixth column gives the rate of increase, D', of the corrected viscosity. This is obtained by dividing the increase of viscosity over that of the previous measurement by the increase in the molal concentration of ammonia. The average value of D' is the rate of increase over the whole interval between zero concentration of NH_3 and the concentration of NH_3 which is nearest to 5-molal.

It is known from the lowering of the partial pressure of ammonia over such solutions as the above,¹ that the ammonia is to some extent bound by the metal salts, but the viscosity curves obtained by us show a not very great deviation from the curve of the viscosity when ammonia is added to pure water. Of course the complexes formed by these metals and ammonia are far less stable and not so well defined as the complexes with copper, silver, and zinc; still the interesting fact is that instead of getting a negative viscosity effect here, there is a slight increase in the viscosity.

This is the important evidence of the new work, that such unstable complexes as are formed between ammonia and lithium, potassium,

¹ Gans, *Z. anorg. Chem.*, 25, 236 (1900). Abegg and Riesenfeld, *Z. physik. Chem.*, 40, 84 (1902). Riesenfeld, *Ibid.*, 45, 461 (1903).

ammonium and calcium salts are somewhat more viscous and must therefore be larger, or less symmetrical, than the ordinary complexes of the same salts with water in simple aqueous solutions.

It is not easy to assign a reason why salts of silver, copper and zinc, on the one hand, should show a preference to form compact complexes with ammonia, and, on the other hand, lithium, potassium, ammonium and calcium salts should show a preference to form compact complexes with water. Various analogies suggest themselves, for example, the difference between the sulfo- and the oxy-salts. Thus, tin, arsenic, and antimony show a marked tendency to form well defined sulfo-salts but very poorly defined oxy-salts; on the other hand, chromium and manganese show no tendency to form sulfo-salts, but they do form well defined oxy-salts, as in the chromates and permanganates.

To compare with the viscosity values for ammoniacal aqueous solutions, it seems of great importance to obtain the values for solutions in anhydrous ammonia, both with and without small additions of water. Work in this direction has already been begun in this laboratory.

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TWO NEW AND VERY DELICATE TESTS BY USE OF THE REAGENT, "TETRAMETHYL BASE."

BY ROBERT J. CARNEY.

Received November 16, 1911.

An acetic acid solution of the organic base, tetramethyldiaminodiphenylmethane, $(\text{CH}_2)_4\text{N}_2(\text{C}_6\text{H}_4)_2$, was used by Trillat¹ in 1903 for the detection of traces of lead and manganese. His method is to convert the metals into the form of dry sulfates, then warm and treat with a few drops of a solution of sodium hypochlorite, remove the chlorine by washing and add the reagent and warm. A beautiful blue color develops, which disappears on cooling and reappears on warming. With manganese it is not necessary to add the hypochlorite, but merely to add sodium hydroxide and ignite before adding the reagent. Trillat found that this gave a very delicate test for both lead and manganese.

This base has also been used as a reagent for the detection of ozone in mixtures containing hydrogen peroxide and the oxides of nitrogen. For this purpose the base is dissolved in alcohol, and strips of paper are moistened with the alcoholic solution and held in the gas. Ozone gives a violet color, nitrogen dioxide a straw-yellow and hydrogen peroxide no color whatever. Arnold and Mentzel² were the first to use the reagent for this purpose. They named the reagent "tetra base," but

¹ *Compt. rend.*, 136, 1205-1207; also *J. Chem. Soc. Abstr.*, 1903, 512.

² *Ber.*, 35, 1324.

finding later that *p*-phenylenediamine had long been sold under this name, they changed the name to "tetramethyl base." Fischer and Marx,¹ Fischer and Braehmer,² and Kaiser and McMaster³ have also used this reagent in their work as a test for ozone.

A modification of Trillat's method has been used for some time in this laboratory as a test for manganese, confirming the results obtained by inorganic tests. The base is prepared as follows: Warm on the water bath for one hour a mixture of 30 grams of dimethylaniline, 10 grams of formaldehyde, 200 cc. of water, and 10 cc. of sulfuric acid. After cooling, make alkaline with an excess of sodium hydroxide, drive off the unchanged dimethylaniline with steam. Filter after cooling, wash the brownish product with water, then recrystallize once from alcohol. This gives a pure, yellowish white product.

There are objections to the use of an acetic acid solution of the base, as recommended by Trillat. The acetic acid solution should be heated when used, but when heated the base immediately precipitates and will not dissolve until the solution is cooled. A colorless acetic acid solution of the base is hard to obtain. It is unstable and soon darkens, even though kept away from the light. The use of citric acid as the solvent has been found to be much more satisfactory. The reagent is made up by dissolving 2.5 grams of the organic compound in a solution of ten grams of citric acid in 10 cc. of water. This solution is then diluted to 500 cc. It is perfectly colorless, will not give a precipitate upon heating even to boiling, and is stable, no precautions with regard to keeping out light being necessary.

With any compound of lead or manganese in which the metal has a valence of more than two, a cold solution of the reagent will give a deep reddish purple color due to an oxidation product of the reagent. Cobaltic and nickelic hydroxides also cause the formation of the color, although the reaction takes place perhaps somewhat more slowly and the color is not as deep usually as with manganese or lead. This test finds application in any of the ordinary systems of qualitative analysis. If the metals of the ammonium hydroxide group are separated from each other by the use of sodium peroxide or sodium hydroxide and hydrogen peroxide, the manganese which precipitates in this group will remain with the ferric hydroxide. If no cobalt or nickel is present, the ferric hydroxide precipitate may be tested for manganese by washing it and pouring a small quantity of the reagent over it. The filtrate will have a deep reddish purple color, if manganese is present. The original ammonium hydroxide precipitate may be tested for manganese by washing

¹ *Ber.*, 39, 2555.

² *Ibid.*, 39, 940-68.

³ *Am. Chem. J.*, 39, 96.

it thoroughly and allowing it to stand with free access of air for several minutes, then adding the reagent to a portion of the precipitate. Cobalt and nickel do not interfere. In the ammonium sulfide group, the manganese sulfide may be dissolved in cold, dilute hydrochloric acid, the hydrogen sulfide boiled out, and manganese separated from zinc by the use of sodium hydroxide and bromine water. The precipitate of manganese dioxide should be thoroughly washed and if cobalt and nickel are absent, the solution of the organic reagent may be poured over it. If cobalt or nickel is present, the precipitate should be dissolved in hydrochloric acid with the addition of peroxide, if desired, and the manganese separated by the action of ammonium hydroxide and hydrogen peroxide. The resulting precipitate is washed and tested with the reagent. Another way of carrying out the test is to boil out the hydrogen sulfide from the hydrochloric acid solution of manganese sulfide, then add sodium hydroxide in excess, filter, wash thoroughly, let stand a few moments and add the reagent. A rapid test for manganese, which may be used upon a solution containing all of the ordinary metals, consists in boiling the acidified solution to remove chlorine or other halogen, then adding sodium hydroxide in excess, filtering the precipitated hydroxides, washing, allowing to stand about ten minutes and then adding the reagent. Lead, cobalt, nickel and other elements give no colorations.

Use of Reagent as a Test for Gold.—No mention has ever been made of the action of this reagent upon salts of gold. With very dilute solutions of gold chloride, the reagent gives a very beautiful purple color, due to the oxidizing action of the gold salt; this soon changes to blue and then becomes colorless. The blue color reappears upon warming. With more concentrated solutions the color is purple by transmitted light and bluish to green by reflected light. It was found by working with very dilute solutions that this reagent affords a very delicate test for gold, not interfered with by platinum, palladium, or other elements. The color is very much more distinct than "purple of Cassius." Free mineral acid interferes with the reaction. Solutions should be neutralized and made slightly acid with acetic or citric acid. To determine the delicacy of the test, a gold solution was made up by dissolving 20 mg. of metallic gold in nitrohydrochloric acid. This was evaporated to remove chlorine, neutralized with sodium carbonate and made slightly acid with acetic acid. The solution was then diluted to one liter. Portions of this solution were diluted to 50 cc. and tested with the reagent. The following table gives the results:

Au solution.		Grams of gold.	Result.
Cc.			
25		0.0005	Very fine purple color.
5		0.0001	Good blue color.
1		0.00002	Plainly visible light blue.
0.5		0.00001	Barely visible light blue.

The delicacy of the test in a solution containing nothing but gold is 0.01 mg. per 50 cc.

Use as a Test for Ammonia.—The test for ammonia makes use of the fact that hydrogen peroxide has no action upon a solution of a manganous salt unless an alkali is present. In the presence of even a trace of alkali the peroxide instantly oxidizes the manganese to a brown higher oxide. The test is carried out by heating the solution supposed to contain the ammonium salt with sodium hydroxide in an Erlenmeyer flask fitted with a rubber stopper through which passes a short glass tube bent at right angles. A piece of filter paper is moistened with a solution made up by dissolving 2 grams of manganous sulfate in 200 cc. of water and adding 5 cc. of the ordinary laboratory hydrogen peroxide solution. This filter paper is held directly in front of the tube through which the steam and ammonia are passing. If ammonia is present in any quantity a brown stain will appear upon the paper. This stain may be moistened with a drop of the organic reagent, and a deep purple color will appear. The excess of hydrogen peroxide present has no effect upon the test. With exceedingly small quantities of ammonia, no brown stain will be formed, but a purple stain will readily be obtained upon adding the reagent. Steam itself has no action if manganous sulfate is used. If manganous acetate is used, very slight purple stains may form even when no ammonia is present. To test the delicacy of this test, a solution of ammonium chloride was made up containing 63 mg. of ammonium chloride per liter, which would be equivalent to 20 mg. of ammonia per liter. The following table gives the results obtained:

NH ₄ Cl solution. Cc.	Grams NH ₃ .	Result.
25	0.0005	Very distinct brown color. Very brilliant purple stain.
5	0.0001	Faint brown color. Very brilliant purple stain.
2.5	0.00005	Faintly visible brown color. Good purple stain.
1	0.00002	No visible brown stain. Distinct purple spot.
0.5	0.00001	Slight bluish spot.
Steam alone		No coloration.

It is possible then by this method to easily detect 0.02 mg. of NH₃ and by carrying out carefully to be able to detect 0.01 mg.

THE ELECTROCHEMICAL OXIDATION OF SOME HYDRAZINE SALTS.¹

BY J. W. TURRENTINE AND WILLIS A. GIBBONS.

Received December 1, 1911.

The investigation here reported embraces the electrochemical oxidation of hydrazine carbonate, and of the two halogen compounds of hydrazine, the chloride and bromide, as obtained under various conditions of electrolysis. The original plan of the work included also the study of the oxidation of hydrazine iodide. The results obtained with the other two halogen compounds of hydrazine, however, made the proposed electrolysis of the iodide appear of doubtful profit.

In connection with his study of the electrolysis of the hydronitrogens, Szarvasy² observed the behavior of hydrazine hydroxide, sulfate and chloride. He found that under the conditions which were obtained during his experiments there was no evidence of the formation of oxidation or reduction products of hydrazine other than nitrogen and hydrogen, respectively, and that these products were evolved at the anode and cathode, respectively, in the ratio of 1 : 2. This is obviously the proportion theoretically resulting from the quantitative decomposition of that substance into its elements. In explanation of the formation of these electrode products, the authority cited states that the hydrazine cations were discharged at the cathode, there "reacting with two molecules of water, forming hydrazine hydrate, and liberating hydrogen." At the anode, he explained, the hydrazine was oxidized. The presumption is that the hydrogen of the hydrazine molecule was taken up by the liberated oxidizing agent at the anode and that nitrogen was evolved. Where the hydroxide or the sulfate was electrolyzed, the oxidizing agent evolved at the anode was presumably oxygen, and where the chloride was electrolyzed, the oxidizing agent was free chlorine. The products of oxidation were then, in the first two cases, nitrogen and water, and in the third case, nitrogen and hydrochloric acid.

The condition of the solution employed with respect to its acidity or neutrality is not mentioned, nor can one infer, except in the case of the solution of the hydroxide, what that condition was, as either the neutral or mono-acid, or the acidic, or di-acid, salt may have been employed.

In the belief that a wider variation in conditions of electrolysis, the conditions at the anode being made to simulate oxidizing agents of varying activity or intensity, would yield oxidation products other than nitrogen and water, one of us³ electrolyzed hydrazine sulfate in solutions of varying degrees of acidity, with the current density at the anode vary-

¹ From the thesis of Willis A. Gibbons presented to the Faculty of Wesleyan University in partial fulfilment of the requirements for the M.A. degree.

² *J. Chem. Soc.*, 1900, 603.

³ Turrentine, *Am. Chem. Soc., Proc.*, New Haven, July, 1908.

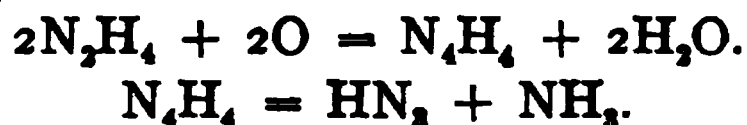
ing between very high and very low values, and the temperature varying between the boiling point of the solution and zero degrees. The anode reactions were followed, not through observing the ratio of the volumes of gas evolved at the anode and cathode, respectively, but rather by examining the solution, and the vapors coming therefrom, for hydronitric acid.

In these experiments no hydronitric acid was obtained at any temperature during the electrolysis with currents giving low current densities at the anode, nor at high temperatures with high current densities at the anode. However, with high current density and low temperature, and with saturated solutions of the sulfate of hydrazine, strongly acidified with sulfuric acid, there was an abundant evolution of hydronitric acid observable on distillation.

The conditions prevailing during these experiments, together with the results obtained, justified the belief that the electrochemical oxidation of hydrazine here obtained was a secondary oxidation, rather than a primary. Under conditions of low temperature and high current density, the electrolysis of solutions of high concentration in the sulfate ion leads to the production of the persulfate ion. The latter is capable of oxidizing hydrazine to hydronitric acid.¹

The oxidation of hydrazine by chemical means has been shown to yield only nitrogen and water,² or in addition to these, ammonia or ammonia and hydronitric acid,³ depending on the nature of the oxidizing agent.

Browne and Shetterly⁴ have made an elaborate study of the chemical oxidation of hydrazine, using a variety of oxidizing agents and determining the nature and amounts of the oxidation products obtainable with each. The results obtained by these investigators have enabled them to effect a classification of the various oxidizing agents studied into three groups: (a) Those "oxidizing agents such as hydrogen peroxide, potassium chlorate, and potassium persulfate [which] decompose hydrazine sulfate in acid solution, yielding varying amounts of some such intermediate condensation product as 'Buzylene,' $\text{HN} : \text{N.NH.NH}_2$, or 'aminotriimide,' which in turn decomposes with formation of hydronitric acid and ammonia." The two stages of this reaction may be represented by the two equations:



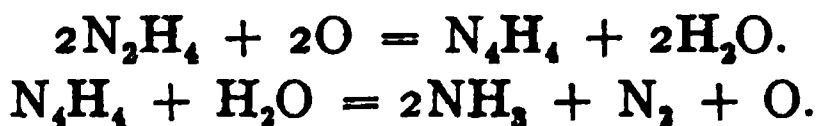
¹ Browne and Shetterly, *THIS JOURNAL*, 31, 221 (1909).

² Rimini, *Gazz. chim. ital.*, 29, I, 265 (1899); *Atti. accad. Lincei Roma*, [5] 15, II, 320; *Chem. Zentr.*, 1906, II, 1662. Browne and Shetterly, *THIS JOURNAL*, 30, 53 (1908).

³ Browne and Shetterly, *Loc. cit.*, et al.

⁴ *THIS JOURNAL*, 29, 1305 (1907); 30, 53 (1908); 31, 221 (1909).

(b) Those "oxidizing agents, typified by potassium permanganate, manganese dioxide, and ferric oxide [which], decompose hydrazine sulfate in acid solution yielding varying amounts of some such intermediate condensation product as 'tetrazone,' $\text{H}_2\text{N.N} : \text{N.NH}_2$, which breaks up under the conditions of the experiment with the formation of nitrogen and ammonia." The following equations are offered to represent these reactions:



(c) Those "oxidizing agents, as for example potassium iodate, mercuric oxide, and mercuric chloride [which], decompose hydrazine sulfate in acid solution at a temperature of 100° apparently without formation of intermediate condensation products." The reactions of this class of oxidizing agents may be represented by the equation



An additional conclusion resulting from this investigation is quoted: "In general, it may be said that the progress of the reaction in any case is very largely influenced by the temperature, by the concentration of the hydrazine, of the sulfuric acid or the alkali, and of the oxidizing agent, by the potential of the oxidizing agent, and by the methods adopted in bringing the substances together." The interesting observation is made that the production of NH_3 and HN_3 by the oxidation of N_2H_4 by the halogen compounds conforms with the periodic arrangement of the halogens in the particular, that, with the increasing atomic weight of the halogens, the yield of these oxidation products decreases. Thus chlorates yield ammonia and hydrochloric acid, while bromates yield less of them, and iodates, none at all.

In the light of the results obtained in the electrochemical oxidation of the sulfate of hydrazine, and in the chemical oxidation of this compound, it did not appear improbable that an electrochemical oxidation of the halides and of other compounds of hydrazine could be effected in which an oxidation simulating that of the first or second class of oxidizing agents could be produced. In case a direct electrochemical oxidation could not be induced which would simulate the oxidizing agents of the first or second class, it was deemed probable that an indirect electrochemical oxidation could be brought about through the formation of anode products which would act as oxidizing agents of the desired class. This possibility was probably realized in the electrochemical oxidation of hydrazine sulfate. The experiments of Szarvasy would indicate that the oxidizing influences existing at the anode under the conditions of his experiments analogized an oxidizing agent of the third class. These influences, under suitable control, should lead to the formation of oxidizing agents of any one of the three classes which should react subse-

quently, though perhaps practically simultaneously, with the hydrazine ion.

The investigation of the chemical oxidation of hydrazine has shown that while an oxidizing agent applied under one set of conditions acts as a member of one class, when applied under entirely different conditions it may act as a member of a different class. It does not follow, then, from this consideration that because the electrochemical oxidation under one set of conditions may be classified with the third group of oxidizing agents, that obtained under entirely different conditions may not act as a member of one of the other groups of oxidizing agents.

To produce those conditions electrochemically simulating a decrease in the active mass of a chemical oxidizing agent, the current density at the anode should be decreased. The relative active mass of this agent, so to speak, may be still further decreased by increasing the active mass of the reducing agent with which it is to react. This may be accomplished by stirring the solution undergoing electrolysis, best by rotating the anode. While, of course, this procedure does not increase in the solution the actual concentration of the substance undergoing oxidation, it does very greatly increase its concentration within the zone of oxidation in the immediate neighborhood of the anode.

The "potential" of the oxidizing agent at the anode can be influenced probably only by varying the electrolyte, or the relative concentrations of the several electrolytes present—as by increasing or decreasing the relative concentrations of the different anions.

Temperature may be controlled with ease within certain limits. With increasing current densities, however, it is increasingly difficult to prevent a rise in temperature in the immediate proximity of the electrode and in the entire solution. Thus, by electrochemical means we are able to vary the temperature, the concentration of the hydrazine (the substance undergoing oxidation), the acidity or alkalinity of the solution undergoing electrolysis, the intensity of the oxidation influences at the anode simulating the oxidizing agents, and, within limits, also their "potential."

The Electrochemical Oxidation of Hydrazine Carbonate.

Constan and Hansen¹ prepared percarbonate by electrolyzing a saturated solution of potassium carbonate at low temperatures and with a current yielding a high current density at the anode. The electrochemical oxidation is probably analogous to that whereby persulfate is prepared from sulfate. Percarbonates have been shown to decompose in water solution with the formation of hydrogen peroxide and the primary carbonate. It was deemed possible that by the electrolysis of a saturated solution of hydrazine carbonate at low temperatures and high current

¹ *Z. Elektrochem.*, 3, 137 (1896); 3, 443 (1897).

densities, hydrazine percarbonate, a substance hitherto unprepared, might be formed. While it was not expected that the compound would be sufficiently stable to permit of its being recovered in the form of a solid, its formation in solution, it was thought, might be accomplished in a manner similar to that in which hydrazine persulfate was prepared by electrochemical oxidation.

The existence of conditions at the anode favorable to the formation of percarbonate of hydrazine would have been evidenced by an evolution of oxygen there, as such an evolution would have shown that the hydrazine was not undergoing quantitative oxidation. Or the evolution of gas there in amounts less than that called for by the theoretical, quantitative oxidation of the hydrazine to nitrogen and water, should have indicated the possible formation of percarbonate. This volume of nitrogen arising from the oxidation of hydrazine to nitrogen and water should equal the volume of oxygen consumed in that oxidation, as is evident from the equation



The volume of anode gases, then, should have equaled one-half of the cathode gases. Furthermore, the presence of percarbonate should have led to the formation of hydrogen peroxide, which, being an oxidizing agent of the first order, should have produced ammonia and hydronitric acid from its action on the hydrazine. Evidence of the oxidation of hydrazine carbonate to percarbonate could have been gotten, then, both from the ratio of the anode to the cathode gases, and from the products obtained on distillation of the hydrazine carbonate under the proper conditions. Doubtless the N_2H_5^+ (or $\text{N}_2\text{H}_6^{++}$) cation is more easily oxidized than is the CO_3^{--} anion. However, one might rely on the migratory tendencies of the cation cathode-ward to remove it from the region of primary oxidation immediately surrounding the anode.

Experimental.

A solution of hydrazine carbonate was prepared by treating hydrazine sulfate, in saturated solution, with more than the equivalent amount of barium hydroxide, also in saturated solution. Carbon dioxide was then passed to saturation and the precipitate of barium sulfate and carbonate was filtered off. The resulting solution was evaporated over a low flame to a thick syrup. Curtius¹ prepared the carbonate of hydrazine by evaporating the aqueous solution of the carbonate *in vacuo* and likewise obtained a syrup, which he described as caustic. One of us, by carrying the evaporation still further, obtained a solid which was resinous or varnish-like.

The electrolytic cell consisted in a cylindrical glass vessel 2.5 cm. in diameter and 6.5 cm. deep. This was provided with a tightly fitting

¹ Curtius and Jay, *J. prakt. Chem.*, [2] 39, 27.

two-holed stopper, through which capillary tubes were inserted. The platinum wires which were to constitute the electrodes were sealed through the walls of the capillary tubes and entered the cell through them. To one capillary tube was sealed a section of glass tubing, 2.5 cm. long and 0.5 cm. in diameter, which constituted the cathode compartment. The end of the other capillary tube was flush with the lower surface of the stopper. The platinum wire which entered through it encircled the cathode compartment and constituted the anode. The capillary tubes were joined to Hempel gas burettes. The cell was connected in series with an oxy-hydrogen gas coulometer and an ammeter.

The cell was filled to a suitable depth with the syrupy hydrazine carbonate and under it was then placed a Dewar beaker containing a mixture of solid carbon dioxide and alcohol. The temperature of the bath was maintained at -25° – -30° . The electrolysis, effected by a current of 1–1.5 amp. in strength, was conducted for several minutes in order that the evolved gases might displace the air in the cell and tubes. A stronger current was deemed prohibitive because of the difficulties of perfect refrigeration. The electrode gases were collected and analyzed and their volumes compared with one another and with those obtained from the coulometer.

Numerous experimental difficulties were encountered, among which were those incidental to the frothing of the viscous electrolyte and the difficulty of equalizing the gas pressures in the two electrode compartments. The results obtained from the comparison of gas volumes alone showed conclusively that the oxidation at the anode was of the hydrazine, exclusively, and not of the carbonate, ions, unless, indeed, the percarbonate was formed but then reacted quantitatively with the hydrazine. Only nitrogen, with perhaps a trace of oxygen, was evolved there.

The Electrochemical Oxidation of the Neutral Hydrazine Chloride.

Hydrazine dihydrochloride was prepared in solution by treating a known amount of hydrazine sulfate in hot, saturated solution, with an equivalent amount of barium chloride, also in hot, saturated solution. The barium sulfate formed was removed by filtration. The filtrate, after having been tested to show its freedom from both barium and sulfate ions, was neutralized with sodium hydroxide. A portion of this solution was diluted to an approximately two per cent. concentration, calculated on the basis of the neutral, or monohydrochloride of hydrazine. The value of this solution in hydrazine was then determined accurately by analysis of portions of it by the method of Rimini.¹

The apparatus employed was simple and consisted of an electrolytic cell, constructed of a tall, narrow beaker, of 200 cc. capacity. The cathode consisted of a short section of platinum wire. This was immersed

¹ Rimini, *Loc. cit.*

to a depth of something over a centimeter, thus affording a very small active surface, in order that the reduction there might be reduced to a minimum. In those experiments where the anode was held stationary, a piece of platinum foil constituted that electrode. This was suspended in the solution and was supported on the edge of the beaker. Its proximity to the cell wall made it probable that only one face of it was sufficiently active to be considered in computing current density. Where the anode was rotated, a circular disc of platinum gauze was employed. This was 4 cm. in diameter and was supported by a thick wire of the same material fastened perpendicularly to its center. By means of this stem the anode was suspended in the solution from the vertical axis of a small electric motor.

The procedure in general consisted in the electrolysis of a known volume of the analyzed solution of hydrazine hydrochloride for such a length of time as would afford an oxidation of a suitable proportion of the hydrazine present. The length of time required then depended on the current density. The course of the oxidation at the anode was followed, as in the case of the sulfate, by observing the ammonia and the hydronitric acid formed, rather than by determining the nature and the ratio of the gases evolved at the respective poles. Justification for this procedure lay in the fact that it was less laborious and required much less complication of apparatus, and that the only stable oxidation products of hydrazine, with the exception of nitrogen and water, the more common products, are ammonia and hydronitric acid. The formation of these, we have seen, may be accounted for on the supposition that other hypothetical oxidation products are formed which, because of their lack of stability, break down into these products. Thus, both fact and hypothesis may be construed to support this procedure.

At the completion of the electrolysis, the solution was removed from the cell and, in cases where its volume had been changed by evaporation, it was diluted to its original volume. It was then analyzed in aliquot portions and the decrease in value in hydrazine was noted.

A measured volume of the electrolyzed solution was transferred to a distilling flask, 10 cc. of concentrated sulfuric acid were added through a dropping funnel, and the solution was distilled to a volume of about 10 cc. The distillate and the uncondensed gases were led by means of an adapter into a solution of silver nitrate containing sodium acetate to decrease the formation of free nitric acid.

The precipitate found in the receiver (AgCl and AgN_3) was filtered on a tared Gooch filter, was washed, dried at 105° , weighed and its weight noted. It was then washed with hot nitric acid, containing one part of concentrated nitric acid to four parts of water, to dissolve out any

¹ Dennis and Isham, *THIS JOURNAL*, 29, 18 (1907).

silver trinitride present.¹ After again washing and drying, the precipitate was reweighed and any loss in weight, representing AgN_3 , was noted. As a further check on this observation, the nitric acid solution which had passed through the precipitate was tested with hydrochloric acid for the presence of the Ag^+ ion.

Other portions of the solution were acidified with sulfuric acid and treated with potassium iodate in sufficient amount to oxidize completely any hydrazine remaining therein. This oxidizing agent has been shown to yield no ammonia when employed in this way. The solution was then distilled for ammonia in the usual way and the evolved ammonia was caught in a known volume of standard acid. The theoretical yield of ammonia was based on the equation, proposed by Browne and Shetterly to represent the oxidation of hydrazine to ammonia and hydro-nitric acid,



In calculating the yield, only that hydrazine was considered which the analysis subsequent to the electrolysis showed had been oxidized. In the following paragraphs are given briefly the more important experimental details. The condition of electrolysis designated by "low temperature" may be taken to mean 0° – 10° , and by "high temperature," 50° – 60° . Current density at the anode (a. c. d.) is expressed in amperes per square centimeter.

Experimental Details.

Experiment 1.—Conditions: Low temp., low c. d., stationary anode. Vol. of soln., 175 cc.; time, $6\frac{1}{2}$ hours; current, 0.05–0.075 amp.; a. c. d., 0.003; oxidation, 22.1 per cent.; no NH_3 or HN_3 present.

Experiment 2.—Conditions: Low temp., low c. d., rotating anode. Vol. of soln., 100 cc.; time, 3 hours; current, 0.1 amp.; oxidation, 21 per cent; no NH_3 or HN_3 present.

Experiments 3–5, Inclusive.—Conditions: Low temp., high c. d., stationary anode. Vol. of soln., 170 cc.; time, 58 minutes, 40 minutes, 30 minutes, respectively; current, 1 amp.; a. c. d., 0.05; oxidation, 75 per cent., 66 per cent., 65.5 per cent., respectively; no NH_3 or HN_3 present.

*Experiment 6.—*A solution made up from the residues from the three preceding experiments was electrolyzed to the point of complete oxidation of the hydrazine, as evidenced by the evolution of Cl_2 at the anode, and by subsequent tests with KIO_3 in acid solution. Analysis showed the absence of HN_3 and the presence of traces of NH_3 .

Experiment 7.—Conditions: Low temp., high c. d., rotating anode. Vol. of soln., 164 cc.; time, $3\frac{3}{4}$ hours; current, 1–1.5 amp. Cl_2 was being evolved at the end of the electrolysis; however, the analysis of the soln. for N_2H_4 showed that the oxidation had amounted to only 95 per cent. This observation is of interest as indicating that it is possible for N_2H_4 and Cl_2 (or hypochlorous acid?) to exist together in soln., provided the concentration of the former be sufficiently low. No HN_3 or NH_3 was present.

¹ Dennis and Isham, *Loc. cit.*

² THIS JOURNAL, 29, 1305 (1907), see p. 1310.

Experiment 8.—Conditions: High temp., low c. d., stationary anode. Vol. of soln., 150 cc.; time, 3 hours; current, 0.076 amp.; oxidation, 7.1 per cent.; no NH_3 or HN_3 present.

Experiment 9.—Conditions: High temp., low c. d., rotating anode. Vol. of soln., 160 cc.; time, 2 hours; current, 0.1 amp.; oxidation, 11.1 per cent.; no NH_3 or HN_3 present.

Experiments 10–12, Inclusive.—Conditions: High temp., high c. d., stationary anode. Vol. of soln., 150 cc. in Experiment 10, 200 cc. in Experiments 11 and 12; time, 2 hours, $2\frac{3}{4}$ hours, $1\frac{1}{4}$ hours, respectively; current, 1–1.5 amp.; a. c. d., 0.05–0.075; oxidation, 49 per cent., 85.88 per cent., 34.36 per cent., respectively; no HN_3 present. Analysis for NH_3 (25 cc. portions): *Experiment 10*, vol. of stand. acid taken, (a) 25 cc., (b) 25 cc.; stand. alkali, to neutralization point, (a) 18.29 cc., (b) 18.26 cc.; vol. of acid neutralized by NH_3 (1 cc. stand. acid = 1 cc. stand. alkali), (a) 6.71 cc., (b) 6.74 cc.; NH_3 present, per cc., (a) 0.000457 g., (b) 0.000458 g.; yield in NH_3 , (a) 71.7 per cent., (b) 71.9 per cent. *Experiment 11*, vol. of stand. acid, (a) 26.0 cc., (b) 26.0 cc.; vol. of alkali to neutralization point, (a) 19.26 cc., (b) 19.2 cc.; vol. of acid neutralized by NH_3 , (a) 6.75 cc., (b) 6.8 cc.; NH_3 present, per cc., (a) 0.0004595 gr., (b) 0.000462 g.; yield in NH_3 , (a) 36.6 per cent., (b) 36.9 per cent. *Experiment 12*, vol. of standard acid, each (a and b), 25 cc.; vol. stand. alkali (average of two), 20.81 cc.; acid neutralized by NH_3 , 4.19 cc.; NH_3 present, per cc., 0.000284 g.; yield in NH_3 , 60.55 per cent.

Experiment 13.—Conditions: High temp., high c. d., rotating anode. Vol. of soln., 150 cc.; time, $1\frac{1}{2}$ hours; current, 1.5 amp.; a. c. d., 0.05. An evolution of Cl_2 was noticeable at the end of the electrolysis. Oxidation, 95.75 per cent.; no HN_3 present. Analysis for NH_3 (25 cc. portions): vol. of stand. acid (a) 25 cc., (b) 25 cc.; vol. of standard alkali, to neutralization point, (a) 18.4 cc., (b) 18.9 cc.; vol. of acid neutralized by NH_3 , (a) 6.6 cc., (b) 6.7 cc.; NH_3 present, per cc., (a) 0.000449 g., (b) 0.000456 g.; yield in NH_3 (aver. of two), 30.67 per cent.

The Electrochemical Oxidation of the Neutral Hydrazine Bromide.

A solution of hydrazine carbonate was prepared in the manner already described. A water solution of hydrobromic acid was then added in the requisit amount. The solution was analyzed for hydrazine, by the method of Rimini, and was then diluted to a 2 per cent. concentration.

The method of Rimini obviously cannot be applied to the analysis of hydrazine as hydrobromide, or in the presence of bromide, unless a suitable correction be made for the reduction of the iodate by the bromide ion. The value of the standard iodate solution was determined in terms of the bromide ion by analyzing a solution of potassium bromide of known content. This standardization was conducted in an exactly similar manner to that prescribed by the method of Rimini for the determination of hydrazine by iodate. The solution of hydrazine bromide was then analyzed for the bromide ion by precipitation, under suitable conditions, with silver nitrate. From the weight of the resulting silver bromide was calculated the bromide content of the hydrazine solution, and, from that, the correction which would have to be introduced in the results obtained from the analysis of portions of the same solution for hydrazine.

The apparatus employed and the procedure observed in the electrochemical oxidation of hydrazine monohydrobromide were the same as those which have been described under the account of the parallel experiments with hydrazine hydrochloride. In each of the experiments, details of which follow, the volume of solution subjected to electrolysis was 200 cc.

In every experiment the analysis for hydronitric acid gave negative results.

Experimental Details.

Experiment 14.—Conditions: Low temp., low c. d., stationary anode. Time, 11½ hours; current, 0.11 amp.; a. c. d., 0.005; oxidation, 27.1 per cent; no NH_3 present.

Experiment 15.—Conditions: Low temp., low c. d., rotating anode. Time, 5 hours; current, 0.05 amp. The percentage oxidation in the experiment was so slight that NH_3 and HN_3 were not tested for.

Experiment 16.—Conditions: Low temp.; high c. d., stationary anode. Time, 2 hours; current, 1–1.5 amp.; a. c. d., 0.05–0.075; oxidation, 47.2 per cent; no NH_3 or HN_3 present.

A second analysis for HN_3 was made in which the modification was introduced of adding solid Ag_2SO_4 to the solution about to undergo distillation for HN_3 . The silver salt was added in sufficient amount to combine with all the bromide ions present and thus prevent the distillation of HBr . This modification was introduced in order that NH_3 , by the formation of AgN_3 in the receiver of the condenser, might be detected in smaller amounts. When Ag_2SO_4 was employed, no precipitate at all appeared in the receiving solution, indicating the absence of HN_3 .

Experiment 17.—Conditions: Low temp., high c. d., rotating anode. Time, 3½ hours; current, 1.25 amp.; oxidation, 57.7 per cent.; yield in NH_3 , 10.4 per cent.

Experiment 18.—Conditions: High temp., low c. d., stationary anode. Current, 0.11 amp.; a. c. d., 0.005; oxidation, 41.9 per cent.; yield in NH_3 , 39.8 per cent.

Experiment 19.—Conditions: High temp., high c. d., stationary anode. Current, 1–1.5 amp.; a. c. d. 0.05–0.075; oxidation, 66.6 per cent.; no NH_3 present.

Experiment 20.—Conditions: High temp., high c. d., rotating anode. Time, 2½ hours; current, 1–1.5 amp.; oxidation, 68 per cent.; yield in NH_3 , 9.1 per cent.

Discussion of Results.

A survey of the results obtained from the electrochemical oxidation of hydrazine hydrochloride shows (a) that no hydronitric acid is obtained from any solution, whatever the conditions may have been under which the oxidation was effected; (b) that only nitrogen and water (or hydrochloric acid) are obtained at low temperatures, and at low current densities, whatever the other conditions may have been; and (c) that only the combination of high temperature and high current density lead to the formation of ammonia; under these conditions a very satisfactory yield is obtained. The rotation of the electrode, under the conditions of current density observed in these experiments, appeared to have but little, if any, effect. It may be remarked that the evolution of gas from the electrode itself effects pretty efficient stirring.

There is no circumstance in Expts. 1–8 which would encourage the be-

lief that the oxidation of hydrazine electrochemically to ammonia is a matter of "potential" of the oxidizing agent, or of the rate at which the oxidizing agent, or influence, is administered to the hydrazine. Whether the potential of the oxidizing influence at the anode changes or not is a matter of conjecture. While the solution undergoes a change from neutrality to acidity, it is probable that the solution in immediate contact with the anode is always acid. A state of acidity would result there whether the reaction be an oxidation of the nature represented by the equation



or a "chloridation" of that, represented by the equation



as both reactions remove the base. And it is doubtful if the most efficient stirring obtainable experimentally would reduce this condition to zero. These considerations would rather discount the idea of a change of potential. If the change in temperature effected a change in potential, this should have been evidenced in Expts. 9 and 10, unless the oxidizing agent at this potential requires in addition a certain active mass, produced at high current density, to oxidize hydrazine to ammonia and hydro-nitric acid, realized in Expts. 11-14.

An accumulation of hypochlorite ions in the neighborhood of the anode would lead to the evolution of oxygen there with a lowering of anode potential. A high current density and a low temperature would be favorable to this condition. Such a change, if occurring, produced no result different from that realized in other experiments where such a condition was less probable.

The high current density in Expts. 9 and 10 is only relatively high, being limited by the increasing difficulty of refrigeration by ordinary refrigerants, and a much higher current density might have resulted in producing other oxidation products. Expts. 1-10, inclusive, would indicate that a rise in temperature is not able to change the order of the oxidation under the set of conditions observed. Why a still higher temperature was not maintained will become apparent later. There is, then, but little evidence to support the supposition that the change in oxidation products is effected through a change in potential of, or in the rate of production of the oxidizing agents at the anode, or in the temperature at which they are produced. An explanation is obtainable, however, from the consideration of the secondary reactions which occur in general at the anode when chlorides are electrolyzed.¹ Hypochlorite, stable at

¹ A supposition that the N_2H_6^+ ion undergoes a further dissociation yielding an anion in which nitrogen exists alone is not here advanced, although it is strongly suggested by the extreme readiness with which nitrogen is evolved from solutions containing this ion. Such a dissociation would be analogous to that attributed to the

low temperatures, results when neutral or slightly acid solutions of chlorides are electrolyzed. Its formation may result through the interaction of water and discharged chlorine, or of the OH^- ion and discharged chlorine. The production of free OH^- ion within the solution, through the discharge of H^+ ions at the cathode, and their possible participation in the anode reactions, need hardly be considered in view of the rapidly increasing acidity within the solution during the electrolysis. When the concentration of the ClO^- ions becomes sufficiently high, oxygen may be liberated at the anode, which then oxidizes hypochlorite to chlorate. Thus, at low temperature, a high concentration of hypochlorite is essential to the formation of other oxy-chloride compounds. Free chlorine evolved at the anode could react with hydrazine or, in case that were not immediately available, with water, to form in the former case, hydrochloric acid, with liberation of nitrogen, and in the latter case hypochlorous acid. Hypochlorite would undoubtedly react with hydrazine in a manner approximating that of nascent chlorine. So, as long as the hydrazine is present in any considerable amount, the concentration of the ClO^- ion will be kept low and the electrochemical formation of chlorates prohibited. The chemical oxidation of hydrazine by chlorine has been shown to yield little or no ammonia and hydronitric acid, when allowed to react under the most favorable conditions. It is therefore readily understood why no ammonia and hydronitric acid should be formed under the conditions obtaining in Expts. 1-8, inclusive.

At higher temperatures the anode products may be quite different as the result of secondary reactions. In slightly acid solutions of hypochlorite at a temperature of 50° , hypochlorous acid oxidizes the hypochlorite ion to chlorate, as represented by the equation



This is a reaction of low velocity.

In Expts. 9 and 10 the temperature is favorable to the formation of chlorates. On account of a low current density the formation of hypochlorite is slow and the chances for a high concentration in hypochlorite ions correspondingly poor, both on account of the slow formation of the hypochlorite and the speed of the reduction of it by the hydrazine present. The yield in chlorate, then, and in ammonia and hydronitric acid should be practically *nil*. The conclusions conform with the results.

However, in Expts. 11-14, inclusive, where both a high current density and a high temperature are maintained, it is conceivable that there

OH^- ion whereby O^{--} ions are produced and the evolution of oxygen at the anode during the electrolysis of certain solutions is so satisfactorily explained.

¹ Foerster, *J. prakt. Chem.*, 59, 53 (1899); 63, 141 (1901). *Z. Elektrochem.*, 9, 6 (1903). Thomsen, *J. prakt. Chem.*, 59, 244 (1899). Kretzschmar, *Z. Elektrochem.*, 10, 789 (1904).

hypochlorite forms at a sufficiently great rate to acquire a concentration high enough to react with the formation of chlorate, a reaction favored by the temperature. By a tertiary reaction, then, hydrazine is oxidized to ammonia and hydronitric acid.

At low temperatures and in slightly acid or neutral solution the chlorate and the hydrazine ion may exist simultaneously, as both the mono- and the dichlorate have been formed and crystallized from aqueous solution.¹ In hot solution, however, it is doubtful if they can so exist without mutual interaction.

If the foregoing explanation of the result obtained in these experiments is the correct one, low concentration in hydrazine is favorable to those reactions which are proposed in explanation of the formation of ammonia and hydronitric acid. More interesting results could not be looked for, then, for the electrolysis of solutions more concentrated in hydrazine.

The supposed action of chlorate on the hydrazine has been spoken of as yielding both ammonia and hydronitric acid, or as belonging to the first class of oxidizing agents. However, no hydronitric acid was found. This fact is explainable by either of two suppositions: the chlorate under the conditions of these experiments acted as an oxidizing agent of the second class and produced only ammonia; or, more probably, hydronitric acid was formed but was subsequently decomposed electrochemically through the discharge of the N_3^- ion at the anode.

In Expts. 14–20, where the bromide is electrolyzed, the results obtained do not conform so well with theory based on the known behavior of discharged bromide ions.

As the bromide ion may be discharged at a low potential, it is probable that no oxygen is evolved at all. The reaction whereby the hydrazine is bromidized may be represented by the equation



In the electrolysis of bromides the formation of bromates from hypobromites takes place with much greater readiness than the analogous reactions which occur when chlorides are electrolyzed. Therefore, the formation of bromates is not so readily controlled or retarded by conditions and it is less easy to say that they would or would not form under this or that set of conditions—the conditions being those which were obtained in the experiments under discussion. There is reason to believe that the oxidation occurring in those experiments where ammonia was formed was effected by bromate and not by hypobromite. Furthermore, while bromate is more readily formed in solution under various conditions of electrolysis than is chlorate, and for that reason should have been found in larger amounts, it is more reactive with hydrazine at all temperatures

¹ Salvadori, *Gazz. chim. ital.*, 37, 32 (1907).

and in its oxidation of that substance yields smaller amounts of ammonia and hydronitric acid than the chlorate.

The reasons for not subjecting the iodides of hydrazine to the same study are now apparent; both iodine¹ and iodate,² under all conditions tested, are oxidizing agents of the third class and therefore can be expected to yield no interesting products.

Summary.

1. The electrochemical oxidation of hydrazine carbonate, under conditions which favor the formation of percarbonates, results in the quantitative oxidation of the hydrazine.

2. That of hydrazine hydrochloride and hydrobromide yields only nitrogen and water or, in addition to these, also ammonia, depending on the conditions of the electrolysis.

3. The reactivity of hypochlorites with hydrazine appears to preclude the possibility of the formation in the presence of hydrazine in large amounts of the more highly oxidized oxy-chlorine ions.

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NOTES.

A Jointless Stock-Bottle-Support Buret.—It is believed that with the apparatus herein described and figured, titration will be made easier, more economical of solutions, and (especially with caustic alkalies) more accurate, than with other apparatus, for the reasons that (1) exposure to the air and (2) the difficulties of transferring the solution back and forth between container and buret are reduced to a minimum.

Since the first draft of this article was made, the apparatus of Burkhardt³ has appeared, which, however, though similar in principle, is believed to be not so good as the one herein described; because of (1) the *joint* wet by the solution, (2) the closed-in top to the buret, (3) the metal brace below, and (4) the arrangement of the opening above, which would seem to make it difficult to empty the buret back into the container.

As the diagram shows, our apparatus consists essentially of a *container-limb* (made experimentally from a tall open-mouthed cylinder), joined above by a short, wide, unobstructed, nearly horizontal tube, to a *buret-limb* (made experimentally from a 50 cc. buret shortened to a net (measuring) capacity of 15 or 20 cc.).

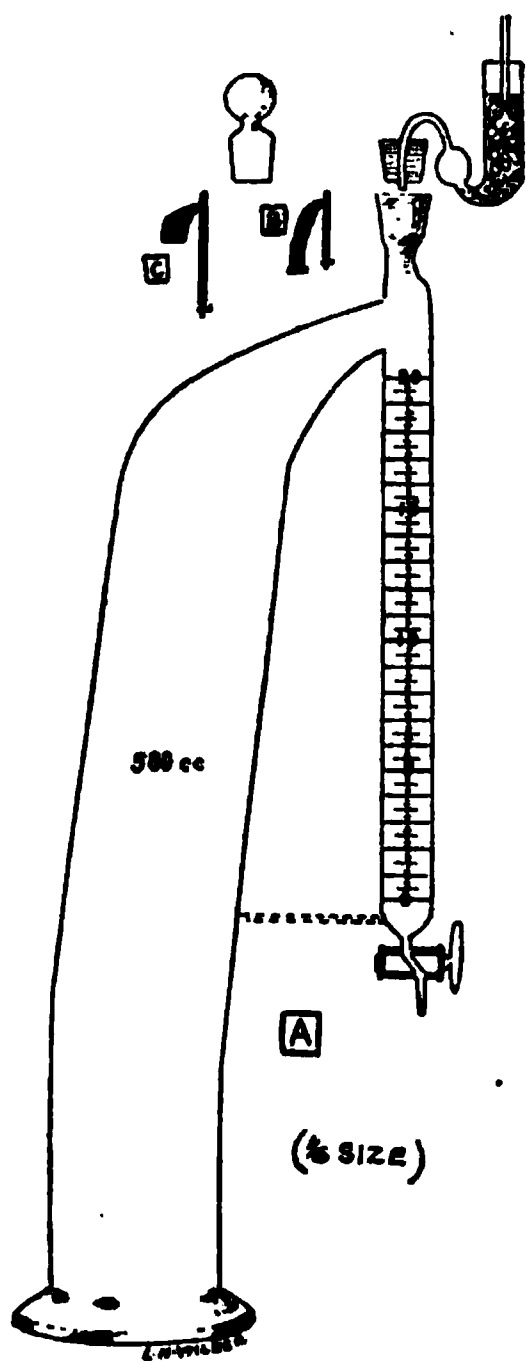
In transferring the solution from container to buret, or *vice versa*, the apparatus is tipped to an almost horizontal position, with the limb from which the liquid is to flow, uppermost. To facilitate this transfer, the

¹ Browne and Shetterly, *THIS JOURNAL*, 30, 53 (1908).

² Rimini, *Loc. cit.*

³ *Chem. Ztg.*, 35, 656; *C. A.*, 5, 20, 3359.

two limbs must be inclined at a slight angle to one another, diverging from above downward; and, as the buret must be vertical while in use, the container is made to assume a slight slant by an almost imperceptible bend a short distance above the base.



In the most generally useful form of the apparatus (A), the tip of the buret is 3–6 inches above the supporting surface. This necessitates a tall container and a short buret. If it is desired to have the buret of full or extra length without extreme elongation of the container, the apparatus may be proportioned as shown in the small silhouettes (B) or (C) in the figure. In these forms the apparatus must be supported on a block or shelf during the titrations.

It adds to the strength of the apparatus at its weakest point, though it is not absolutely necessary, to seal in a glass-rod brace as indicated by the dotted lines in the figure. The upper opening should be slightly flared and glass-stoppered, similarly to a volumetric flask. A rubber stopper with a small soda-lime tube should also be provided. The constriction just below the opening is to reduce the chance of

spilling while the liquid is being transferred from one tube to the other.

The apparatus may be of almost any dimensions; a very handy size for ordinary desk work is: Height, 45 cm.; diameter of base, 10 cm.; container-limb, 500 cc.; buret-limb, 20 cc. net, tip 13 cm. above supporting surface. We have also in use (as part of a very compact portable CO₂-in-air apparatus) a unit (form B) of the following dimensions: Height, 26 cm.; container-limb, 150 cc.; buret-limb, 10 cc. net.

The obvious advantages of this form of titration apparatus may be summarized as follows: Compact, self-contained and (form A) self-supporting. Members short and stout. No rubber, metal, or other perishable substance—all glass. No joints, except the single simple stopcock of the buret. No air-pressure or suction; the bodies of liquid in the two limbs separated, or easily transferred in either direction, by gravity; hence no need for running the solution remaining in the buret to waste, and no excuse for allowing the buret to stand idle with solution in it. After the original filling of the container, there is no further exposure of any part of the solution to outside air except as each measured portion leaves the tip of the buret.

By reason of these advantages, this apparatus is believed to be particu-

larly useful for alkalies, especially if provided with an obliquely-bored or otherwise alkali-resistant stopcock.

This apparatus may be had, of any specified dimensions, from Eimer & Amend.

NORMAN ROBERTS.

HYGIENIC LABORATORY, WASHINGTON, D. C.

Filtration with Alundum Plates.—Filtration of large volumes of liquids containing very fine precipitates, by means of asbestos fiber and the Witte plate, has been found very inconvenient at times.

As substitutes for filter plates and asbestos, disks made of "alundum" (fused aluminium oxide) have shown great efficiency. These filter disks were made by the Norton Co., of Worcester, Mass., according to the design, as shown in the accompanying sketch.

An ordinary flat rubber band stretched around the filter disk or plate makes it fit snugly to the funnel, when suction is applied by means of the filter pump. These plates may be had in several grades with pores of different sizes, those with the smallest pores retaining the finest precipitates perfectly. Their use saves the trouble of preparing asbestos and also makes it possible to stir the precipitates without danger of dislodging the filtering material as when asbestos is used.

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THE RELATION BETWEEN THE CONFIGURATION AND ROTATION OF THE LACTONES IN THE SUGAR AND SACCHARINIC ACID GROUPS.

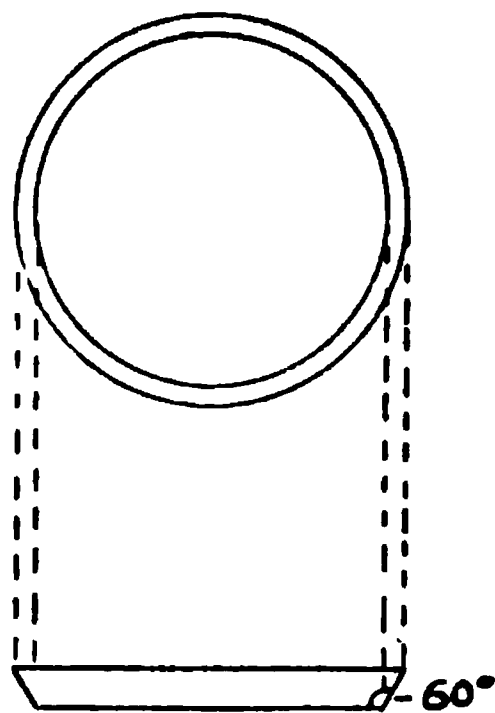
BY HENRY ANDERSON.

Received October 17, 1911.

Hudson¹ has pointed out a very simple relation between the configuration and rotation of the lactones of mono-basic sugar acids, namely, lactones of dextro rotation have the ring on one side of the structure, lactones of levo rotation have it on the other. This relation is true not only for the lactones described by Hudson but for practically all monobasic and some dibasic acid lactones in the sugar and saccharinic acid groups. In the following table are collected the configurations and specific rotations of eighteen such lactones.

¹ THIS JOURNAL, 32, 338.

Fig. 1.



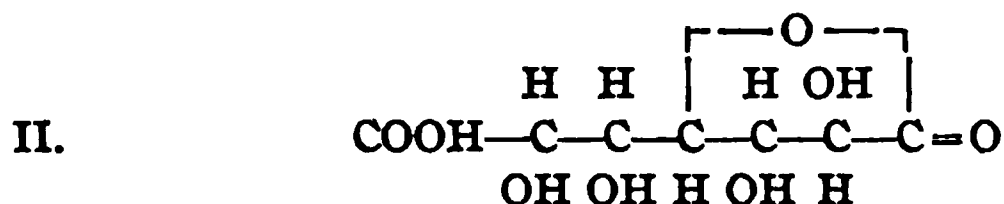
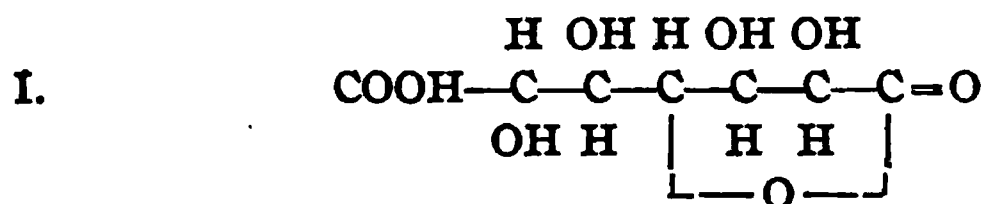
Substance.	Configuration.	Rotation.	Ring position.
α -Galacto-metasaccharin ¹	$\begin{array}{ccccccc} & & & \text{O} & & & \\ & & & & & & \\ & \text{H} & & \text{H} & \text{H} & & \\ & & & & & & \\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & \text{H} & \text{H} & \text{OH} & & \end{array}$	-45.3°	above
β -Galacto-metasaccharin ¹	$\begin{array}{ccccccc} & & & \text{O} & & & \\ & & & & & & \\ & \text{H} & & \text{H} & \text{OH} & & \\ & & & & & & \\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & \text{H} & \text{H} & \text{H} & & \end{array}$	-63°	above
β -Galacto-metasaccharonic ¹	$\begin{array}{ccccccc} & & & \text{O} & & & \\ & & & & & & \\ & \text{H} & & \text{H} & \text{OH} & & \\ & & & & & & \\ \text{CO.OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & \text{H} & \text{H} & \text{H} & & \end{array}$	-98°	above
<i>l</i> -Manno-saccharic ²	$\begin{array}{ccccccc} & & & \text{O} & & & \\ & & & & & & \\ & \text{OH} & & \text{H} & \text{H} & & \\ & & & & & & \\ \text{O}=\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & & \text{H} & \text{H} & & \text{OH} & \\ & & & \text{O} & & & \end{array}$	-201°	above
<i>d</i> -Saccharic ³	$\begin{array}{ccccccc} & & & \text{OH} & \text{H} & \text{OH} & \text{OH} \\ & & & & & & \\ \text{CO.OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{H} & & \text{H} & \text{H} & & \\ & & & & & & \\ & & & & \text{O} & & \end{array}$	$+38^\circ$	below
Glucuronic ⁴	$\begin{array}{ccccccc} & & & \text{OH} & \text{H} & \text{OH} & \text{OH} \\ & & & & & & \\ \text{CHO}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{H} & & \text{H} & \text{H} & & \\ & & & & & & \\ & & & & \text{O} & & \end{array}$	$+19^\circ$	below
β -Dextro-metasaccharin ⁵	$\begin{array}{ccccccc} & & & \text{H} & \text{H} & \text{H} & \text{OH} \\ & & & & & & \\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & & \text{H} & \text{H} & & \\ & & & & & & \\ & & & & \text{O} & & \end{array}$	$+8^\circ$	below
α -Dextro-metasaccharin ⁵	$\begin{array}{ccccccc} & & & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & & \\ \text{CH}_2\text{OH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & & \text{H} & \text{OH} & & \\ & & & & & & \\ & & & & \text{O} & & \end{array}$	$+25^\circ$	below
β -Dextro-metasaccharonic ⁶	$\begin{array}{ccccccc} & & & \text{H} & \text{H} & \text{H} & \text{OH} \\ & & & & & & \\ \text{COOH}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} & & & & & & \\ & \text{OH} & & \text{H} & \text{H} & & \\ & & & & & & \\ & & & & \text{O} & & \end{array}$	-4.7°	below

¹ Nef, *Ann.*, 376, 1.² Fischer, *Ber.*, 24, 539. This substance is a di-lactone, both rings agree with Hudson's hypothesis.³ Sohst and Tollens, *Ann.*, 245, 10. The ring is below for both carboxyl groups. It probably has the position given.⁴ Fischer, *Ber.*, 24, 521.⁵ Nef, *loc. cit.*⁶ Nef, *loc. cit.* This is an exception to the hypothesis. However, the sodium salt of this acid rotates -35° and the dextro rotation, due to lactone formation, is not strong enough to overcome this levo rotation.

Substance.	Configuration.	Rotation.	Ring position.
<i>d</i> -Allonic ¹	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & \text{OH} & & \text{OH} & \text{OH} & & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	-6.8°	below
<i>d</i> -Lactonic ²	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{OH} & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & \text{OH} & & \text{OH} & \text{H} & & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+35^\circ$	below
<i>a</i> -Hydroxymethyl- <i>d</i> -gluconic ³	$ \begin{array}{ccccccc} & & & & \text{CH}_2\text{OH} & & \\ & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & \text{OH} & & \text{H} & \text{OH} & & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+$	below
<i>l</i> -Threo-C ₆ -metasaccharin ⁴	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{H} & \text{H} & & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+43^\circ$	below
<i>d</i> -Erythro-C ₆ -metasaccharin ⁴	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{H} & \text{OH} & & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+55^\circ$	below
<i>a</i> -Hydroxymethyl- <i>d</i> -lyxonic ⁴	$ \begin{array}{ccccccc} & \text{H} & \text{OH} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{H} & & \text{CH}_2\text{OH} & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+82^\circ$	below
<i>a</i> -Isosaccharin ⁴	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{H} & & \text{CH}_2\text{OH} & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+63^\circ$	below
<i>a</i> -Saccharin ⁴	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{OH} & & \text{CH}_2 & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+93^\circ$	below
<i>a</i> -Hydroxymethyl- <i>d</i> -arabonic ⁵	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{OH} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & =\text{O} \\ & & & \text{OH} & & \text{CH}_2\text{OH} & \\ & & \text{---} & \text{O} & \text{---} & & \end{array} $	$+72^\circ$	below

¹ Levene and Jacobs, *Ber.*, 43, 3141. This is an exception to the hypothesis.² Levene and Jacobs, *loc. cit.*³ Kiliani, *Ber.*, 19, 1914. Nef, *loc. cit.*⁴ Nef, *loc. cit.*⁵ Spoehr, *Am. Chem. J.*, 43, 235.

The above-described relation between configuration and rotation affords a new method for determining the configuration of the lactones formed by some dibasic acids. Thus, β pentahydroxy pimelic¹ acid forms a mono lactone which has either configuration, I or II.



Since the specific rotation of the lactone is $+68^\circ$, it must have configuration I.

The data given above furnish additional evidence for the hypothesis advanced by Hudson. They show how varied the lactone structure may be and that hypothesis still apply.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

2,5-DIMETHYLHEPTANE.

BY LATHAM CLARKE AND SYDNEY A. BEGGS.

Received November 6, 1911.

In the study of the octanes, which for some years has been in process in this Laboratory, certain relationships have been discovered between chemical constitution and physical properties, an account of which has been included in an earlier paper.² It is of considerable interest to ascertain whether these relationships hold true in the series of nonanes as well as in the series of octanes, and the study of the nonanes has therefore been taken up; meanwhile, the researches on those octanes which are yet to be synthesized are being pushed on as actively as possible. In this paper is given a description of the synthesis and properties of 2,5-dimethylheptane, the first nonane to be prepared in this laboratory.

This hydrocarbon has been made by Mlle. Welt,³ who used the Wurtz reaction; but the compound prepared by her was apparently not at all pure since the boiling point is given as $128-134^\circ$. The 2,5-dimethylheptane prepared in this research boiled at $135.6-135.9^\circ$ at 760 millimeters pressure and had at 15° the specific gravity 0.7190, compared with water at 15° .

The literature records four nonanes in addition to that of Mlle. Welt:

¹ Fischer, *Ann.*, 270, 90.

² THIS JOURNAL, 33, 520 (1911).

³ *Ann. chim. phys.*, [7] 6, 122.

1. Normal nonane.¹
2. 2,6-Dimethylheptane.²
3. 4-Ethylheptane.³
4. 2-Methyl-3,3-dimethyl-4-methylpentane.⁴

As pointed out in the earlier paper on octanes,⁵ the hydrocarbons fall in classes according to their constitution. Thus normal octane stands by itself, the three monomethylheptanes form a class by themselves, as do the four dimethylhexanes, and the physical properties of each of these different classes exhibit certain regularities. To show these a table of the physical constants of the first eight octanes is given herewith.

	Boiling point.		Specific gravity	Index of refraction
	Degrees.	Mm.	15/15.	N _D (25°).
1. Normal octane.....	124.7	at 760	0.7068	1.3963
2. 2-Methylheptane.....	116.0	at 761	0.7035	1.3944
3. 3-Methylheptane.....	117.6	at 760	0.7167	1.4022
4. 4-Methylheptane.....	118.0	at 760	0.7217	1.3978
5. 2,3-Dimethylhexane.....	113.9	at 758	0.7246	1.4075
6. 2,4-Dimethylhexane.....	110.0	at 763	0.7083	1.3986
7. 2,5-Dimethylhexane.....	108.25	at 760	0.6991	1.3930
8. 3,4-Dimethylhexane.....	116.5	at 759	0.7270	1.4038

By substituting a normal chain with an "iso" group, that is, in going from normal octane to 2 methylheptane, we observe a depression in boiling point of 8.7°; but as we move the substituting methyl group along from the 2- to the 3- and again to the 4-position a slight elevation in boiling points occurs. With increasing boiling point, we find a rise in the specific gravity in the case of these three methylheptanes. Considering now the dimethylhexanes, that which has the lowest boiling point is 2,5-dimethylhexane, where we have two "iso" groups, one at each end of the chain. We should expect that since, in the case above noted, we move one methyl group from the 5- to the 4-position, and observe an elevation of boiling point, we should likewise find an elevation of boiling point when we change one methyl group of 2,5-dimethylhexane from the 5- to the 4-position and we do find a slight increase, in the first case 1.6°, in the second 1.75°.

But when we again move our methyl group, this time from the 4- to the 3-position, giving 2-3-dimethylhexane, we get a relatively very considerable rise. Here, however, we have the substituting methyl groups in adjacent positions. In 3,4-dimethylhexane, when again the methyl groups are on adjacent carbon atoms, we observe a still higher boiling point.

¹ Thorpe and Young, *Ann.*, 165, 19 (1873). Krafft, *Ber.*, 15, 1692 (1882).

² Wurtz, *Jahresb.*, 1855, 575.

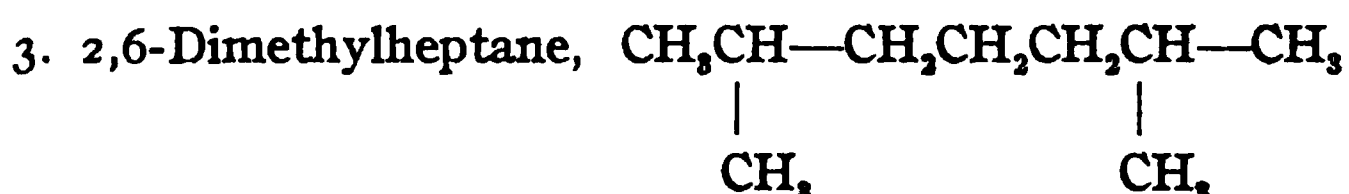
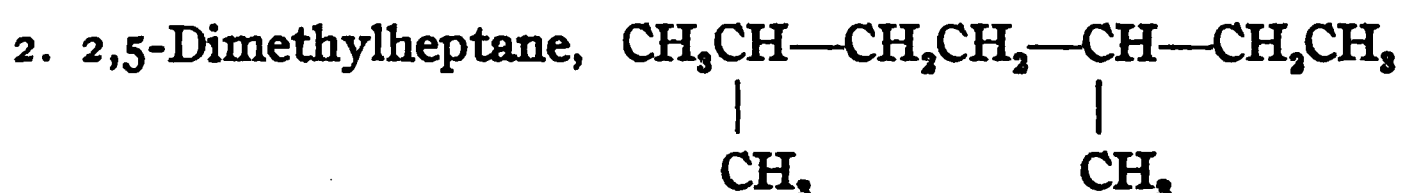
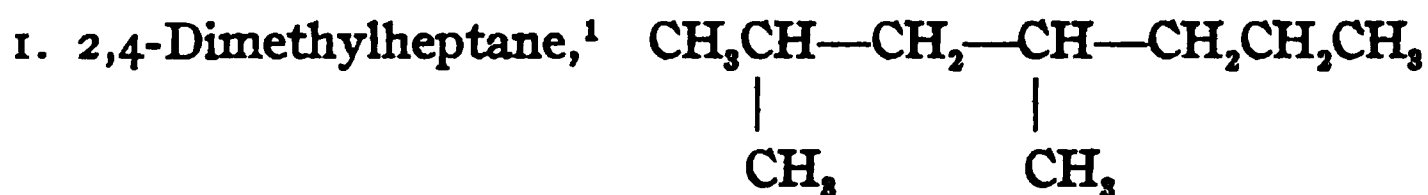
³ Oberreit, *Ber.*, 29, 2003.

⁴ Silva, *Ibid.*, 5, 984.

⁵ *Loc. cit.*

The specific gravities of the methylheptanes rise in relation to the boiling points and the same is true of the dimethylhexanes, without exception, in each class the higher the boiling point, the greater the specific gravity.

Let us now examine the properties of the nonanes. As none of the methyl octanes have yet been made, we cannot include them, but there are three of the dimethylheptanes, *viz*:



	Boiling point.		Specific gravity	Index of refraction
	Degrees.	Mm.	15°/15°.	N _D (25°).
1. 2,4-Dimethylheptane ²	132.9-133	at 752	0.7206	1.4014
2. 2,5-Dimethylheptane ³	135 -135.9	at 760	0.7190	1.4020
3. 2,6-Dimethylheptane ⁴	132		0.7122	..

2,6-Dimethylheptane has the lowest boiling point and the smallest specific gravity. 2,5-Dimethylheptane should by analogy to the octanes come next but, very strange to say, the boiling point is very much higher than we should expect, it being about 3.7° higher, when we should anticipate a difference of about 1.7°, while the specific gravity is about as much greater as we should look for. But in the case of 2,4-dimethylheptane, the boiling point is *lower* than that of 2,5-dimethylheptane by practically 2.7°, and is only one degree higher than that of 2,6-dimethylheptane. This surprising exception is all the more noteworthy, because the specific gravity is normal, that is, somewhat greater than the specific gravity of 2,5-dimethylheptane.

It will be decidedly interesting in view of the above facts to see how the properties of the other nonanes compare and to this end their syntheses will be accomplished as soon as possible, and all attempts to explain postponed until further data are at hand.

¹ An account of the preparation and properties of 2-4-dimethylheptane is given in the succeeding paper.

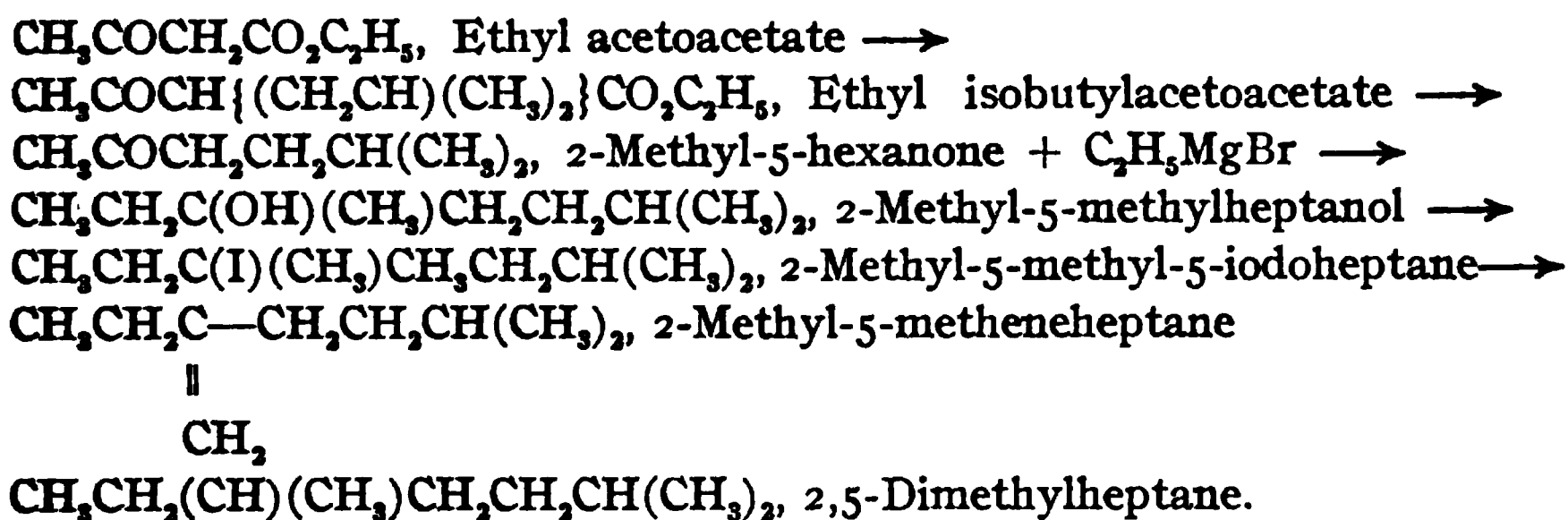
² From data in the succeeding paper.

³ From data determined in this research and given later in the paper.

⁴ Wurtz, *Jahresb.*, 1855, 575. In his paper Wurtz gives the specific gravity at 0° as 0.7247. The value above is a theoretical approximation calculated from Wurtz's figures.

2,5-Dimethylheptane.—The starting point of this research in the synthesis of 2,5-dimethylheptane was ethyl acetoacetate, which was converted into ethyl isobutylacetoacetate by the usual procedure of conversion into the sodium salt and treatment with isobutyl iodide. The ethyl isobutylacetoacetate was then saponified, giving the ketone, 2-methyl-5-hexanone, which was subjected to the Barbier-Grignard reaction, using ethyl magnesium bromide, thus producing an alcohol containing nine atoms of carbon, *viz.*, 2-methyl-5-methyl-5-heptanol. From the last the corresponding carbinol iodide was obtained, and by boiling this with alcohol potash, the nonylene 2-methyl-5-metheneheptane was formed, which was then reduced to 2,5-dimethylheptane.

To summarize these reactions:



Owing to lack of time, the constitution of the nonylene, although probably that given above, was not determined, but the only point in question is the position of the double bond, and since it is reduced to a saturated single bond in the final hydrocarbon, it has nothing to do with the constitution of the nonane.

A noteworthy fact in connection with this nonylene is that it forms a binary mixture with ethyl alcohol which boils at 80° , while the boiling point of the nonylene itself is $139\text{--}140^\circ$. The two liquids are perfectly miscible. This recalls the mixtures of minimum boiling point which normal hexane forms with the lower alcohols.¹

Experimental Part.

Ethyl isobutylacetoacetate, $\text{CH}_3\text{COCH}\{\text{CH}_2\text{CH}(\text{CH}_3)_2\}\text{CO}_2\text{C}_2\text{H}_5$, was prepared from ethyl acetoacetate and isobutyl iodide by the method of Conrad,² the condensation being effected through the sodium salt of the ethyl acetoacetate. The ethyl isobutylacetoacetate was saponified by boiling with a return condenser for eight hours with a 10% solution of caustic potash, using four molecules of caustic potash to each molecule of the acetoacetate. The resulting ketone was distilled with steam, separated, washed with water, dried with calcium chloride and fractionated until the boiling point extended over but one degree, *viz.*, $143\text{--}144^\circ$. The

¹ See page 268, *et seq.*, in "Stoichiometry," by Sydney Young.

² Conrad and Limpach, *Ann.*, 192, 153.

yield of the ketone, which was 5-methyl-2-hexanone, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$, was usually about 40% of the theoretical, 100 grams of the acetate giving 25 grams of ketone. This is not a new ketone, the conditions of preparation only, are new.¹

2,5 - Dimethyl - 5 - heptanol, $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$, 5-Methyl-2-hexanone, a ketone containing seven carbon atoms, was converted into 2,5-dimethyl-5-heptanol containing nine atoms of carbon by the Barbier-Grignard reaction.

Twenty grams of magnesium were dissolved in a mixture of 100 grams ethyl bromide and an equal volume of ether. To this were added ninety-one grams of ketone in an equal volume of ether and the whole heated on the steam bath for one hour. The organo-magnesium compound was then carefully decomposed by ice and water and the mixture neutralized by hydrochloric acid. The ether layer was separated and dried over potassium carbonate. Finally the ether was evaporated off and the remaining liquid fractionated. It gave sixty-one grams boiling from $172-174^\circ$. This was 2,5-dimethylheptanol.

Calculated for $\text{C}_9\text{H}_{20}\text{O}$: C, 75.0 ; H, 13.88

Found: C, 75.11; H, 14.03

Properties: Colorless liquid boiling at $172-174^\circ$. Odor of musty apples. Miscible in the common organic solvents, but not miscible in water.

2,5-Dimethyl-5-iodoheptane, $\text{CH}_3\text{CH}_2\text{C}(\text{I})(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ and its conversion into the nonylene, $\text{CH}_3\text{CH}_2\text{C}-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$,



For the preparation of 2,5-dimethyl-5-iodoheptane, sixty-one grams of 2,5-dimethyl-5-heptanol were mixed with eight grams of red phosphorus and fifty-four grams of iodine and allowed to stand for one hour, after which the mixture was heated on a steam bath for ten hours. The resulting iodide was washed with water and filtered from the unchanged phosphorus but was not distilled.

It was converted into the nonylene without further purification as follows: seventy grams of caustic potash were dissolved in one hundred and five grams ethyl alcohol and seventy grams of the iodide carefully added to the warm mixture. It was then heated on a sand bath for two hours using a reflux condenser. The alcohol and nonylene were next distilled off, the greater part coming over at 80° . By diluting this distillate with water, the nonylene was separated, washed with water and dried over calcium chloride. On boiling the nonylene with sodium there was no tarnishing of the metal, showing that the iodine had been completely removed. On fractionating the liquid, nineteen grams were obtained boiling at $139-140^\circ$.

¹ See Beilstein, *Handbuch*, III Aufl., Bd. I, 1000.

Calculated for C_9H_{20} : C, 85.71; H, 14.29

Found: C, 86.09; H, 13.97

Properties: Colorless liquid with a sweet petroleum-like odor, boiling at 139–140°. Decolorizes bromine in chloroform solution. Miscible with the common organic solvents not miscible with water.

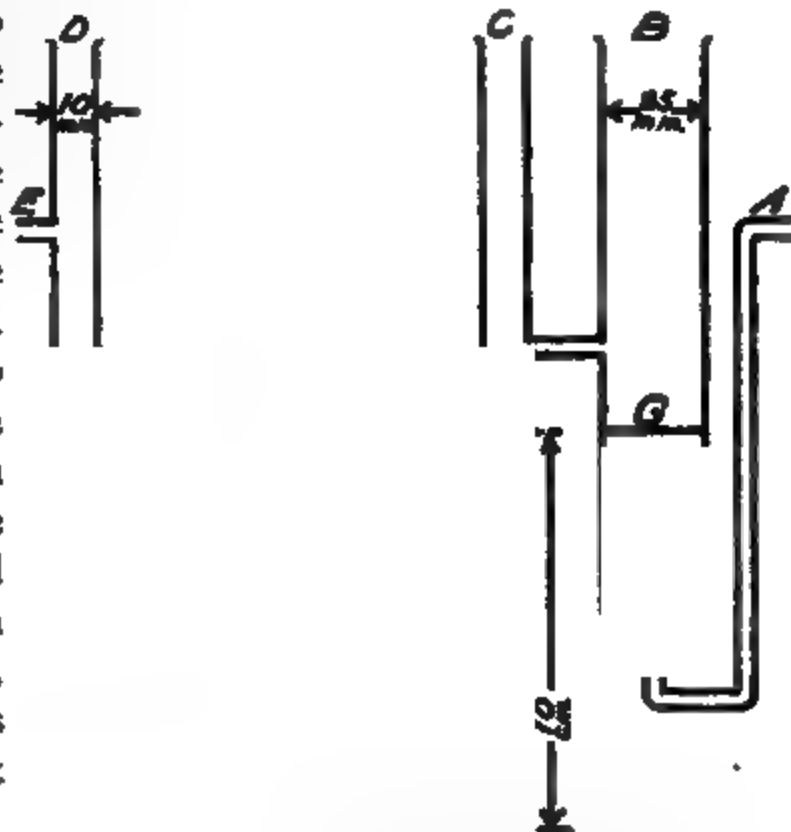
2,5-Dimethyl heptane, $CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_3$, was prepared from



the nonylene by reducing it by Sabatier and Senderens' method of passing the unsaturated hydrocarbon with an excess of hydrogen over freshly reduced nickel at a temperature of 160–180°. The apparatus used is shown in the accompanying diagram and was a modification by Bedford¹ of that used by Sabatier and Senderens. The original article of Bedford is inaccessible to most readers so a description of our apparatus is herewith included.

The apparatus is of glass and is filled to G and F with nickel oxide, deposited on pumice, which was prepared as follows:

Twenty grams of purest nickel nitrate were heated in a nickel crucible over a blast flame for two hours. Pieces of pumice stone cut up to fit into the apparatus were also heated in the blast lamp in a nickel crucible for one hour. After the nickel oxide which was formed had cooled, it was made into a paste by mixing it with a little distilled water free from chlorine. The pieces of pumice were stirred into this until thoroughly coated and then removed with steel forceps, placed on a large watch glass and dried in an air bath at 95° for two hours.



The nickel prepared pumice was then put in the apparatus and C and D were stoppered with cork stoppers. B was stoppered with a cork having one hole through which a small dropping funnel was inserted. A current of hydrogen was then passed through the apparatus from A to E and the apparatus was heated in an air bath at 300° for eight hours. The hydrogen used was made by the action of hydrochloric acid on zinc

¹ "Ueber die ungesättigten Säuren des Leinöls, und ihre quantitative Reduktion zu Stearin säure." Inaugural Dissertation zur Erlangung der Doktor, Halle a.S.

and was purified by passing through a solution of caustic potash, over hot copper gauze and finally over solid caustic potash.

After the nickel had been once reduced by heating at 300° for eight hours in a current of hydrogen, it was necessary to heat again to 300° for one hour each time it was used. The apparatus was then placed in an oil bath at 160 – 180° and the nonylene allowed to drop very slowly (about 6 drops a minute) through the dropping funnel on to G. The nonylene was vaporized and carried by the current of hydrogen entering at A over the nickel in F and out at E where it was condensed by an air condenser.

The nonylene was completely saturated by running it once through the apparatus. The nickel was found to work better if after running a few drops of liquid through the apparatus the first time the nickel was used, the process was stopped, heated up to 300° for an hour and then continued again at 160° . It was also found that the same nickel could not be used for two different substances.

Ten grams of the nonylene gave nine grams of the 2,5-dimethylheptane boiling within one degree. It gave no test for unsaturation. This 2,5-dimethylheptane was fractionated until 4 grams were obtained boiling at 135.6 – 135.9° under 760 mm. pressure.

Calculated for C_9H_{20} : C, 84.37; H, 15.63

Found: C, 84.12; H, 16.14

Properties: Colorless liquid with a petroleum-like odor, boiling at 135.6 – 135.9° under 760 mm. pressure. The specific gravity at 15° is 0.7190 referred to water at 15° . The index of refraction was determined with a fine Pulfrich refractometer, $N_D(25^{\circ}) = 1.4020$. The hydrocarbon is fairly miscible with the common organic solvents.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

2,4-DIMETHYLHEPTANE.

BY LATHAM CLARKE AND SYDNEY A. BEGGS.

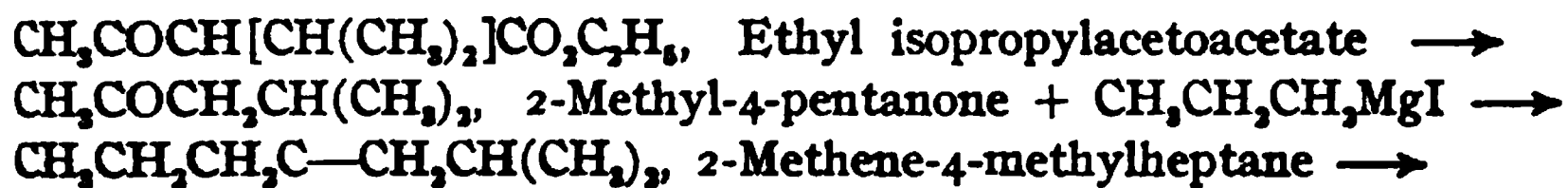
Received November 6, 1911.

This nonane has been synthesized and studied in connection with the researches in this laboratory on the paraffin hydrocarbons.

In the synthesis of 2,4-dimethylheptane, the starting point was ethyl isopropylacetoacetate, which was saponified giving methyl isobutylketone or 2-methyl-4-pentanone. The plan then was to treat the ketone with normal propyl magnesium iodide, which was expected to give an alcohol containing nine atoms of carbon, 2,4-dimethyl-4-heptanol, $CH_3CH_2CH_2C(OH)(CH_3)CH_2CH(CH_3)_2$; the last we intended to convert into the corresponding carbinol iodide, and by then splitting off hydriodic acid by the action of alcoholic potash, the nonylene would be formed

of the formula $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{CHCH}(\text{CH}_3)_2$, which is 4-methene-2-methylheptane.

By reduction of the nonylene, the saturated octane would be produced. We found, however, that when normal propyl magnesium iodide reacted with the above mentioned ketone, the product was the *desired nonylene*, evidently formed from the carbinol, to be expected, by the elimination of one molecule of water. The actual reactions therefore involved in the synthesis of 2,4-dimethylheptane were those of the following summary:



$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$, or 2,4-Dimethylheptane.

The peculiar reaction above noted, where a tertiary alcohol formed in a Barbier-Grignard reaction splits off water to form an unsaturated compound, has not been recorded before in the purely aliphatic series so far as we can find, although cases are known among the aromatic-aliphatic series.¹

Owing to the lack of time the exact constitution of the nonylene was not determined, but it was almost surely that of the ascribed formula. The only thing in doubt, however, is the position of the double bond and this does not affect the constitution of the nonane, as the double bond is saturated in the next step.

Experimental Part.

Methyl isobutyl ketone, $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$, was obtained from isopropyl acetacetic ester by boiling for eight hours with a 10% solution of caustic potash. The ketone was then distilled off with steam, washed with water, dried over calcium chloride and fractionated. From two hundred grams of ester seventy grams of ketone were obtained, boiling at 114–115°.

The nonylene, 2-methene-4-methylheptane, was made from the ketone by treating with an excess of normal propyl magnesium iodide. Twenty-four grams of magnesium were dissolved in 171 grams of normal propyl iodide which had been mixed with an equal volume of ether and 70 grams of the ketone diluted with an equal volume of ether were then added slowly and the whole warmed on a steam bath for two hours. The reaction product was decomposed in the usual manner with ice water and finally with dilute hydrochloric acid. The ether solution was separated

¹ Grignard and Tissier, *Compt. rend.*, 132, 1182 (1901).

and dried over potassium carbonate, the ether was then distilled off and the residue consisting of the nonylene fractionated. The yield was twenty grams of hydrocarbon boiling at 132–133°.

Calculated for C_9H_{18} : C, 85.71; H, 14.29
Found: C, 85.29; H, 14.22.

Properties: Colorless liquid boiling at 132–133°.

Miscible with all the common organic solvents. Immiscible with water. Decolorizes bromine in chloroform solution. It has an odor like that of petroleum.

2,4-Dimethylheptane, $CH_3CH_2CH_2CHCHCHCH_3$, was made from the

$$\begin{array}{c} | \quad | \\ CH_3 \quad CH_3 \end{array}$$

nonylene by reducing it by Sabatier and Senderens' method of passing the vapor of the nonylene with an excess of hydrogen over freshly reduced nickel at 160–180°, after the manner of the reduction of 2-methyl-5-metheneheptane to 2,5-dimethylheptane described in the preceding paper. The nonane was then carefully fractionated with a fifth degree thermometer until five grams were obtained boiling at 132.9–133°.

Calculated for C_9H_{20} : C, 84.37; H, 15.63
Found: C, 84.28; H, 15.92

Properties: Colorless liquid boiling at 132.9–133° at 752 millimeters pressure. It is miscible in the common organic solvents. Does not decolorize bromine in chloroform. Odor of petroleum. Sp. gr. is 0.7206 at 15° compared to water at 15°. The index of refraction was determined with a Pulfrich refractometer $N_D(25^\circ) = 1.4014$.

CAMBRIDGE, MASS.,
October, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VIII.
CAMPHONOLIC ACID AND CAMPHONOLACTONE.

BY WILLIAM A. NOYES, E. E. GORSLINE AND R. S. POTTER.

Received November 23, 1911.

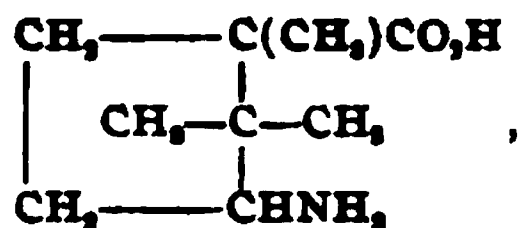
Three lactones are known which correspond to three hydroxy acids which retain the tertiary carboxyl of camphoric acid. These are:

1. Campholactone, obtained by Fitting and Woringer¹ in distilling lauronolic acid and formed when lauronolic acid is warmed with dilute acids.

2. Isocampholactone, first obtained in an impure condition by one of us² in decomposing aminolauronic acid,

¹ *Ann.*, 227, 10.

² *Am. Chem. J.*, 17, 432; 32, 290.

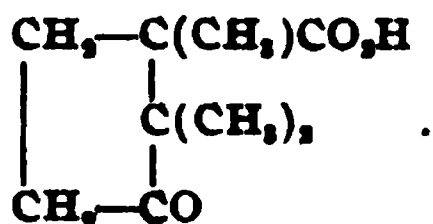


with nitrous acid and later obtained by Bredt¹ by decomposing the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide.

3. Camphonolactone² corresponding to a hydroxy acid formed along with the hydroxy acid of isocampholactone in decomposing the nitroso derivative of aminolauronic acid with sodium hydroxide.³

4. In addition to the three hydroxy acids corresponding to the three lactones a hydroxy acid called hydroxylauronic acid,⁴ which has not been converted into a lactone, has been obtained by the decomposition of the ethyl ester of aminolauronic acid by nitrous acid. The same acid, apparently, is one of the products of the decomposition of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide.⁵ Hydroxylauronic acid has been obtained only as a viscous liquid and the evidence that it is a single, definite compound and not a mixture of two or more hydroxy acids is not very satisfactory.

While structural formulas for some of these lactones and hydroxy acids are to be found in the literature, the formulas which have been given rest on very slender evidence. In the hope of securing more satisfactory evidence for the structure of some one of these acids we undertook, three years ago, the reduction of camphononic acid,



The structure of this acid was demonstrated very conclusively by Lapworth and Lenton.⁶ After several months of work and many futile attempts,

we finally obtained the *amyl ether of camphonolic acid*, $\text{C}_9\text{H}_{14} \begin{array}{l} \text{CO}_2\text{H} \\ \text{OC}_5\text{H}_{11} \end{array}$,

by reducing the camphononic acid with amyl alcohol and sodium. About that time a brief note was published by Bredt⁷ in which he stated that he had effected the desired reduction by electrolytic means. Our own work in this line was, accordingly, discontinued. More recently we have undertaken a careful study of the products obtained by the decomposition

¹ Ber., 35, 1991.

² This name is suggested by Professor Bredt in a private communication.

³ Noyes and Taveau, Am. Chem. J., 35, 385.

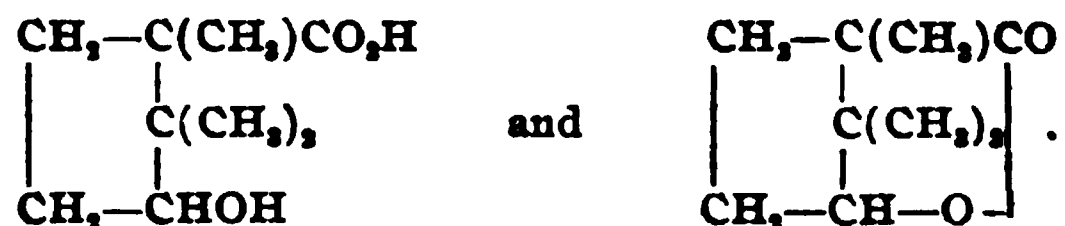
⁴ Am. Chem. J., 18, 687. THIS JOURNAL, 31, 278.

⁵ Am. Chem. J., 32, 289; 35, 385.

⁶ J. Chem. Soc., 79, 1284.

⁷ Ann., 366, 1.

of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide. Among these products Taveau¹ found a lactone melting at 164–165° which gave a hydroxy acid melting at 189.5°.² By comparing the properties of this acid and lactone with those of a sample of the *cis*-camphononic acid and camphonololactone obtained by the reduction of camphononic acid, very kindly sent us by Professor Brecht, we have established the identity of the two substances. We have also oxidized our hydroxy acid to camphononic acid. These compounds must, therefore, have the structures



Experimental Part.

Camphononic acid was prepared by the method of Lapworth and Lenton,³ somewhat modified. Camphanamide (19.7 g.) was dissolved in 10% sodium hydroxide by boiling for a short time. The solution was cooled to 0° and 120 cc. of a solution of 5.4 cc. of bromine in 120 cc. of cold sodium hydroxide (10%) was added. The mixture was allowed to stand 1½ hours at room temperature, was heated for 4 hours on the water bath and was again allowed to stand over night. On the addition of an excess of hydrochloric acid the camphononic acid was precipitated and was filtered off after thorough cooling. It was crystallized from carbon tetrachloride and from water. The yield was about 10 grams but the reaction seems to be very sensitive to slight changes in the conditions. The purified camphononic acid melts at 229–230°; Lapworth and Lenton give the melting point as 228°. In a solution containing 2.4 g. in 100 cc. of benzene $[\alpha]_D = 17.8^\circ$ at 27.5°. In a solution containing 3 g. in 100 cc. of alcohol $[\alpha]_D = -3.9^\circ$.

Reduction of Camphononic Acid. Amyl Ether of Camphononic Acid,



with an upright condenser, ten cc. of amyl alcohol were added through the condenser and then, gradually, 4 grams of camphononic acid dissolved in 20 cc. of amyl alcohol. More alcohol was added as necessary and the boiling continued till all of the sodium had disappeared. The amyl alcohol was distilled with steam, indifferent substances were removed with ether and the reduction product obtained by extracting with ether after acidifying with hydrochloric acid. The acid obtained was a viscous,

¹ *Am. Chem. J.*, 35, 385.

² The values given in the experimental part of this paper are probably more accurate.

³ *J. Chem. Soc.*, 79, 1233.

yellow oil which distilled at 222–223° under a pressure of 40 mm. The analyses indicate that it was mixed with a little unchanged camphononic acid, from which it could not be separated by distillation, but taken with the analyses of salts given below, they leave no doubt as to the character of the compound:

Calculated for $C_{14}H_{20}O_3$: C, 69.4 ; H, 10.7.
 Found: C, 68.3, 68.2, 68.5; H, 9.8, 9.9, 10.2.
 68.7, 69.3 ; 10.1, 10.0.

The calcium salt was prepared by boiling a solution of the acid in dilute alcohol with calcium carbonate. From this solution the copper and silver salts were prepared by precipitation. The analyses gave:

Calculated for $(C_8H_{14} \begin{smallmatrix} \diagup CO_2 \\ \diagdown OC_6H_{11} \end{smallmatrix})_2Cu$: Cu, 11.5; found, 11.4%.

Calculated for $C_8H_{14} \begin{smallmatrix} \diagup CO_2Ag \\ \diagdown OC_6H_{11} \end{smallmatrix}$: Ag, 30.9; found, 31.3%.

Cis-camphonolactone, $\begin{array}{c} CH_2-C(CH_3)-CO \\ | \quad | \quad | \\ C(CH_3)_2 \\ | \quad | \\ CH_2-CH-O \end{array}$.—As stated above, this lac-

tone has been prepared by Bredt by the electrolytic reduction of camphononic acid.¹ Taveau obtained² it by decomposing the nitroso de-

rivative of the anhydride of aminolauronic acid, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ | \\ NNO \end{smallmatrix}$, by boil-

ing it with a 10 per cent. solution of sodium hydroxide. We have prepared it again in a similar manner, using 37.5 cc. of a 33 per cent. solution of sodium hydroxide to 25 grams of the nitroso compound and shaking the mixture for some hours. The bottle containing the mixture was set upright in cold water, to keep it cool, and provided with a stopper bearing a tube which allowed of the escape of the nitrogen which is evolved. The decomposition is very slow at first, owing to the very difficult solubility of the nitroso compound. After some laurolene has been formed, however, it proceeds more rapidly. When the decomposition was nearly complete a second portion of sodium hydroxide and the nitroso compound was added and after some time a third portion. In subsequent decompositions some of the previous mixture was added to hasten the start of the reaction.

After separating the laurolene the mixture of acids formed was precipitated with sulfuric acid and taken up and extracted with ether. The isocampholactone was separated by dissolving the acids in sodium or potassium carbonate and these acids after precipitation a second time were subjected to fractional distillation under the low pressure obtained by a

¹ *Ann.*, 366, 1.

² *Am. Chem. J.*, 35, 385.

Geryk pump. The lactone obtained was about 4 per cent. of the weight of the nitroso compound which was decomposed. We find the melting point of the lactone one or two degrees higher than that given by Taveau and four or five degrees higher than that of the lactone kindly sent us by Professor Brecht, but the following table of comparisons leaves no doubt as to the identity of the compounds:

CIS-CAMPHONOLACTONE.

	From nitroso compound, Noyes and Potter.	Mixture.	From reduction of campho- nonic acid, Brecht.
Melting point.....	165°-167°	163°-165°	161°
$[\alpha]_D$ in alcohol.....	-20.2°		-16.8°
(0.05 g. in 1 cc.).....	at 28°		at 30°
$[\alpha]_D$ in alcohol.....	-22.3°		
(0.1 g. in 1 cc.).....	at 26°		

CIS-CAMPHONOLIC ACID.

	From nitroso compound.	Mixture.	From reduction of camphonic acid, Brecht.
Melting point.....	202°-203°	201°-202°	201°
$[\alpha]_D$ in alcohol.....	+29.2°		+29.7°
(0.1 g. in 1 cc.).....	at 28°		at 30°

	Lactone from nitroso compound.	Mixture.	From our hydroxy acid.
Melting point.....	165°-167°	165°-167°	165°-167°
$[\alpha]_D$ in alcohol.....	-20.2°		-19.8°
(0.05 g. in 1 cc.).....	at 28°		at 28°

Taveau¹ gives the melting point of his hydroxy acid as 189.5°. Professor Brecht² gives the melting point of his acid as 197-198°. The differences are doubtless due to differences in the rate of heating, as the acid is rapidly transformed into the lactone at its melting point or below and slow heating may depress the melting point many degrees. Our thermometer was checked by testing it in boiling paratoluidine and found correct. The melting points were made with an Anschütz thermometer, and there was no stem correction required.

The hydroxy acid was easily converted back to the lactone by heating for fifteen minutes at 255°. The conversion is practically quantitative and the rotation of the regenerated lactone is almost identical with that of the original, indicating that no molecular rearrangement has occurred in the process.

Camphononic Acid from Cis-Camphonolic Acid.—Five-tenths of a gram of camphonolic acid was mixed with 3 cc. of Beckmann's chromic acid mixture³ (twice the theoretical amount) and allowed to stand over night. Two cubic centimeters of dilute sulfuric acid (1 : 1 by vol.) were added and the mixture allowed to stand again for 24 hours. The solution was

¹ *Am. Chem. J.*, 35, 386.

² *Ann.*, 366, 2.

³ *Ibid.*, 250, 325.

diluted, extracted with ether and the camphononic acid was crystallized by dissolving in benzene, evaporating in a test tube on the water bath till crystallization began and adding an equal volume of petroleum ether. The following comparisons with the camphononic acid from camphanamide (see above) establish its identity:

	CAMPHONONIC ACID.		
	From camphanamide by Lapworth's method.	Mixture.	From our hydroxy acid by oxidation.
Melting point.....	229°-230°	227°-228°	227-228°
$[\alpha]_D$ in benzene.....	+17.8°		+17.0°
(0.024 g. in 1 cc.).....	at 27.5°		at 27.5°
$[\alpha]_D$ in alcohol.....	-3.9°		-3.9°
(0.02 g. in 1 cc.).....	at 28°		at 29°

Conclusions.

1. The lactone obtained by Taveau by the decomposition of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide is identical with cis-camphonololactone obtained by Bredt by the reduction of camphononic acid and the corresponding hydroxy acids, camphonolic acid, are also identical.

2. Camphonolic acid has been oxidized to camphononic acid, establishing more completely that this acid contains the hydroxyl group in the same position as the secondary carboxyl of camphoric acid.

3. The amyl ether of camphonolic acid, $C_8H_{14}(OC_5H_{11})CO_2H$, and its copper and silver salts have been prepared. The free acid is a viscous liquid.

4. Cis-camphonololactone melts at 165-167°; $[\alpha]_D$ in alcohol (0.05 g. in 1 cc.) at 28° is -20.2° or at 26° (0.1 g. in 1 cc.) it is -22.3°.

Cis-camphonolic acid melts at 202-203° when rapidly heated; $[\alpha]_D$ in alcohol (0.1 g. in 1 cc.) at 28° is +29.2°.

Camphononic acid melts at 229-230°; $[\alpha]_D$ in benzene (0.024 g. in 1 cc.) at 27.5° is +17.8°; $[\alpha]$ in alcohol (0.02 g. in 1 cc.) at 28° is -3.9°.

URBANA, ILLINOIS.

THE ROLE OF OXIDASES IN THE FORMATION OF CERTAIN CONSTITUENTS OF ESSENTIAL OILS.

[PART I.]

BY BENJAMIN T. BROOKS.

Received October 20, 1911.

The work described in the present paper was undertaken with the object of throwing some light on the manner in which ketones and aldehydes are formed in certain essential oils.

In the study of the essential oil of *Michelia champaca* L.¹ it was noted that an energetic oxidase was present in the flowers, and on investigating

¹ Brooks, THIS JOURNAL, 33, 1763 (1911).

the oil it was found that a considerable quantity of a crystallin ketone, $C_{16}H_{20}O_5$, separated from the oil and that, among other constituents, benzyl alcohol, benzaldehyde and benzoic acid were present. It is believed that these oxidation products owe their existence to the activity of the oxidizing enzyme present in the flowers. Thus, Batteli and Stern¹ and Jaquet² have shown that benzyl alcohol is readily oxidized by an oxidase prepared from certain animal tissues.

According to Lecomte³ the vanilla plant contains an oxidase and the pods richest in vanilla showed the strongest oxidase reactions. He considers that the aldehyde is formed by the oxidation of coniferyl alcohol. Anisic alcohol and anisic aldehyde are present in very small proportions.

The work of the chemists of Roure-Bertrand Fils on oil of peppermint and that of Schimmel and Company on oil of caraway is particularly suggestive. The former chemists have shown⁴ that menthone is formed in *Mentha piperita* chiefly when the plant blossoms and that it is apparently formed at the expense of menthol. Plants systematically deprived of their inflorescences, or affected by parasites so that the blossoms do not develop normally, contain only a very low per cent. of menthone, approximately 3 per cent. instead of 10 to 15 per cent., which is the proportion of the ketone contained in the oil distilled from normal healthy plants. Similar relations were found to hold in the case of absinth,⁵ *Artemisia absinthum* L., and verbena, *Verbena triphylla* L.⁶

It was shown by the chemists of Schimmel and Company⁷ that oil of caraway consists principally of limonene and carvone. Plants deprived of their inflorescences gave neither of these substances. Plants in flower yielded an oil containing limonene and a little carvone while in the oil distilled from mature plants carvone predominated.

The above considerations suggested a search for an oxidizing enzyme in peppermint, caraway and certain other plants which yield essential oils containing ketones or aldehydes as important constituents.

The method of procedure was practically the same for all the plants examined. The fresh plants were ground with clean quartz sand and a little water to a paste, the juice squeezed out through a cloth and then filtered through paper. The reagents used in testing for the oxidase were tincture of guaiac resin, the indophenol reagent of Röhmann and

¹ *Biochem. Z.*, 28, 145.

² *Arch. exper. Path. Pharm.*, 29, 386 (1892).

³ *Compt. rend.*, 133, 745.

⁴ *Bull. Roure-Bertrand Fils.*, [1] 1, 16 (1900); [1] 5, 22 (1902); [1] 8, 31 (1903). Also Charabot, *Compt. rend.*, 130, 518; *Bull. soc. chim.*, [3] 23.

⁵ *Bull. Roure-Bertrand Fils.*, [2] 3, 5 (1906).

⁶ *Ibid.*, [2] 4, 9 (1906).

⁷ Schimmel and Co., *Semi-annual Rep.*, 2, 24 (1896).

Spitzer, phenolphthalin and pyrogallol. Phenolphthalin often gave uncertain results, owing to the dark brown color of the extracts, which color was intensified by the addition of alkali, thus obscuring the pink or red color developed by the alkali and the phenolphthalein formed.

The Oxidase in Carum carvi L.—In the examination of caraway, the green seeds were used. The extract, made as described above, gave positive tests for an oxidase although the reactions were not as pronounced as in the case of the mints, probably owing to the comparatively dry, ripe condition of the seeds employed.

The Oxidase of Peppermint.—The oxidizing enzyme in *Mentha piperita* is localized chiefly in the inflorescence. This is strictly parallel with the results of Charabot on the distribution of menthone in the peppermint plant. The plants were examined for oxidases before and during the flowering period and in the latter case the leaves and inflorescences were tested separately. Before flowering, feeble but positive reactions were obtained. The flower stalks, on the other hand, gave beautiful positive results, the extracts being much more active than extracts of the leaves alone or of the whole plants before the flowering period. Colorimetric comparison of equivalent quantities of extract with equal quantities of reagent was the nearest approach to a quantitative method of several methods that were tried. Pyrogallol was not oxidized by peppermint extract so the quantitative method proposed by Chodat and Bach, depending upon weighing the purpurogallin formed, was not applicable.

In every case in which active solutions were obtained, the activity was lost after standing ten or twelve hours. This behavior is similar to that of the zymase of pressed yeast juice in that the loss in activity of the enzyme is accompanied by a proteolytic digestion of the soluble proteins in the extract. Thus a freshly prepared extract of green peppermint gave a heavy precipitate on heating to 100° , whereas a portion of the same extract, after standing eight hours with a little chloroform as an antiseptic, yielded only a slight turbidity on heating to the same temperature. No evidence was obtained of the presence of a cyano-genetic glucoside. The extract from 400 grams of peppermint flower stalks was allowed to stand 24 hours and then distilled with steam. No trace of hydrocyanic acid was detected in the concentrated distillate by the ferric thiocyanate test.

The instability of the enzyme, in the form of its aqueous extract, rendered uncertain an attempt to oxidize menthol. Fifty cubic centimeters of extract were prepared from 100 grams of peppermint blossoms and to one-half of the extract 2 grams of menthol crystals were added. Both portions of the solution were then shaken in a shaking machine, the air in the apparatus being displaced by oxygen. The absorption of the oxygen was measured by means of gas burettes connected with the ap-

paratus. Both solutions absorbed practically the same amount of oxygen. During the first ten minutes, 8.3 cc. of oxygen were absorbed by each solution, 5.2 cc. during the second ten minutes and thereafter the rate of absorption diminished steadily until after three hours all absorption of gas ceased and the solutions were found to be inactive to the oxidase reagents. The added menthol was recovered by steam distillation and the presence of menthone could not be proven. The action of other oxidases on terpene alcohols will be tested in the continuation of the investigation.

Heating to 100° for a few moments completely destroyed the activity of all the extracts which showed positive reactions for an oxidase.

Precipitation of the enzyme with alcohol, or alcohol and ether gave precipitates which, when filtered off and shaken with water, still showed the oxidase reactions but so greatly diminished in intensity that further purification by this means was not attempted.

It is probable that all of the mints contain such an oxidase, since active extracts were prepared from the flower stalks of *Mentha piperita*, *Mentha viridis*, *Mentha crispa*, *Mentha sylvestris* and *Mentha gentilis*. According to Schimmel and Company,¹ the oil of *Mentha sylvestris* contains a relatively large amount of pulegone. The oil of curly mint, or *Mentha crispa*, contains carvone. It should be noted too that, in addition to menthone, American oil of peppermint has been shown to contain acetaldehyde, isovaleraldehyde and the two acids corresponding to these aldehydes.²

Peppermint extracts which gave strong oxidase reactions contained no peroxides in amounts sufficient to be detected by the starch iodide reaction.

In addition to an oxidase, peppermint plants contain catalase. An extract amounting to 60 cc. was prepared from 25 grams of peppermint blossoms. Five cc. of this extract liberated 42 cc. of oxygen in six minutes from 10 cc. of a 3 per cent. hydrogen peroxide solution.

The presence of catalase in peppermint and other plants considered in this paper makes it extremely improbable that the ketones and aldehydes under discussion result from ordinary hydrogen peroxide oxidation. The occurrence of traces of hydrogen peroxide in green plants is a point in dispute. At any rate it is a fact that when hydrogen peroxide is decomposed by catalase, molecular or inactive oxygen is liberated.³ Thus, tincture of guaiac resin is not colored nor can uric acid or xanthine be oxidized by hydrogen peroxide in the presence of catalase. H. D. Dakin⁴ has recently prepared ketones by oxidation with hydrogen peroxide of saturated fatty acids. He prepared in this way methylnonyl

¹ Schimmel and Co., *Semi-annual Rep.*, 1, 126 (1910).

² Power and Kleber, *Arch. Pharm.*, 232, 639 (1894).

³ Shaffer, *Am. J. Physiol.*, 14, 299 (1905).

⁴ *Am. Chem. J.*, 44, 41 (1910); *J. Biol. Chem.*, 4, 221.

ketone from lauric acid, methylheptyl ketone from caproic acid and methylamyl ketone from caprylic acid. The first two ketones are found as the major constituents in oil of rue and Dakin tentatively suggested that the aldehydes and ketones found in essential oils might be formed in the manner just indicated. The evidence against this hypothesis, for the case under consideration, is as follows: Neither lauric nor caproic acids have been found in oil of rue. Power and Lees¹ found acetic and valeric acids and Houben² detected the presence of a small proportion of caprylic acid. Moreover, Power and Lees found the two corresponding alcohols, n. methylheptyl carbinol and n. methylnonyl carbinol, in oil of rue. Finally, I have shown that ordinary rue, *Ruta graveolens*, contains catalase. The aqueous extract from two grams of the leaves, prepared by grinding in a glass mortar, liberated 65 cc. of oxygen from 10 cc. of 3 per cent. hydrogen peroxide in the short interval of 60 seconds. The formation of these ketones in *Ruta graveolens* by hydrogen peroxide oxidation according to Dakin's hypothesis is clearly not in accord with the facts. It should be noted also that the presence of catalase does not diminish the oxidizing power of the oxidizing enzymes.³

As in the case of the two ketones in oil of rue, the ketones and aldehydes of essential oils are usually found associated with the corresponding alcohols or acids, as menthone and menthol, thujone and thujyl alcohol, citral and linalool or geraniol, benzaldehyde and benzyl alcohol, isovaleraldehyde and isovaleric acid, valeraldehyde and valeric acid⁴ and so on. Also, only open chain ketones or aldehydes may be obtained by Dakin's method, and one carbon atom is split off from the parent substance.

That the oxidation products under consideration may be formed, in certain cases, by autoxidation independent of the action of an oxidizing enzyme, is not entirely excluded, since the formation of aldehydes by autoxidation of the corresponding alcohols, particularly in direct sunlight, has been observed by Neuberg⁵ and others. However, the reaction is quite slow unless catalyzed in some way. This is undoubtedly the function of the oxidases. According to Bach⁶ and others the substance upon which the oxidase acts must be capable of slow oxidation by the oxygen of the air, and the enzyme is assumed to accelerate this reaction. That sunlight alone is not this accelerating factor is highly probable in

¹ *Proc. Chem. Soc.*, 18, 192.

² *Ber.*, 35, 3587.

³ Abderhalden, *Handbuch der Biochem. Arbeitsmethoden*, Berlin, 3, 68 (1910).

⁴ Henderson and Sutherland, *J. Chem. Soc., London*, 99, 1541 (1911), found that isocamphenilic acid could not be formed by oxidation of the corresponding aldehyde by hydrogen peroxide.

⁵ *Biochem. Z.*, 17, 270 (1909).

⁶ *Ber.*, 43, 368 (1910).

view of the results of Ciamician and Silber¹ who have shown that cyclic ketones are invariably split by autoxidation in direct sunlight yielding a series of products not found in natural oils. The readiness with which unsaturated organic compounds undergo autoxidation with the intermediate formation of organic peroxides,² and the rapidity with which essential oils deteriorate through oxidation when kept in poorly stoppered bottles, is well known. Autoxidation alone, however, cannot explain all of the facts observed.

Charabot considered that the more pronounced oxidation, which took place in the inflorescences of the peppermint, was due to the greater respiratory activity of this part of the plant. However, many biological oxidations are known to take place through the medium of oxygen "carriers" and the reactions under discussion are apparently examples of such a process.

The Enzymes in Valerian Root.—Valerian oil contains isovaleraldehyde and isovaleric acid.³ The borneol ester of this acid is one of the major constituents of the oil. Carles⁴ showed that the root also contains an oxidase. An aqueous extract of the ground root does not develop the valerian odor, on standing, if previously boiled. The addition of a little extract brings out the odor and Carles attributed this behavior to the oxidase. I have investigated the question further and have confirmed the experimental work of Carles but I have found that the development of the rancid valerian odor, in the root extract, is due to the liberation of isovaleric acid by a fat splitting enzyme, or lipase. This is shown by the following experiments. On standing a few hours the uncooked extract develops a rancid odor suggestive of free isovaleric acid. As shown by Carles, the odor is not produced in a cooked extract. Addition of emulsin or of potato oxidase does not develop the odor. Dilute sulfuric acid slowly brings out the odor and finally it was found that a small quantity of fresh extract splits ethyl isovalerate, yielding the free acid. Three grams of fresh roots were crushed in a mortar and shaken with 25 cc. of water and two grams of ethyl isovalerate. Two drops of chloroform were added as an antiseptic. After twenty-four hours at approximately 20° the solution was titrated and 0.141 gram free isovaleric acid was found, 16 cc. of *N*/10 alkali being required for neutralization. A control experiment made with a cooked extract showed no free acid. The liberation of the vile and rancid smelling isovaleric acid is, therefore, due to the action of a lipase on the ester and it is probable that one effect

¹ *Ber.*, 40, 2419 (1907); 41, 1071, 1928 (1908); 42, 945, 1510 (1909).

² Engler and Weissberg, *Ber.*, 31, 3046 (1898); 33, 1090 (1900). Dunlop and Schenk, *THIS JOURNAL*, 25, 826 (1903). Brooks, *Phil. J. Sci., Sec. A.*, 219 (1910); *Chemical News*, Jan. 19, 1910.

³ Bertram and Gildemeister, *Arch. Pharm.*, 228, 483 (1890).

⁴ *J. Pharm.*, [4] 12, 148.

of the oxidase is the formation, in the growing plant, of isovaleric acid from isovaleraldehyde, or yet more complicated substances. The free acid must then combine with borneol, since, as shown by the chemists of Roure-Bertrand Fils,¹ esterification of terpene alcohols takes place with *much* greater rapidity in the growing plant than when a mixture of the pure alcohol and acid is allowed to stand. These authors considered that the rapid esterification in the plant was caused by dehydration conditions in the chlorophyll grains and the presence of an enzyme which enabled a state of equilibrium to be quickly reached. They do not mention having investigated any of the plants studied by them for a lipase. The finding of a lipase in valerian supports their hypothesis, although it is possible that the root is not the seat of formation of the borneol isovalerate.

It should be noted also that when old valerian roots are distilled with steam the aqueous distillate contains a considerable quantity of free isovaleric acid, and indeed the acid owes its discovery to this fact.

Oils Containing Thujone.—Oil of tansy, distilled from *Tanacetum vulgare* L., contains a high per cent. of thujone and probably also thujyl alcohol.² An oxidase was prepared from the leaves of this plant by grinding with sand as described above. The reactions with guaiac and the indophenol reagent were particularly sharp.

The essential oil of *Thuja occidentalis* contains thujone and fenchone.³ The leaves also contain an oxidase, as was shown by employing the same methods and reagents noted above. The aqueous extracts contained a large quantity of mucilaginous material and consequently the method of partial precipitation with magnesium sulfate and alcohol, recently recommended by Bach,⁴ was employed to advantage.

Oils Containing Pulegone.—In addition to *Mentha sylvestris*, mentioned above, an oxidase was found in *Satureja montana* L., and *Calamintha officinalis* Muh. The compositions of the essential oils of the two latter species are not accurately known, but as pennyroyal was not available the closely related species *Satureja montana*, having an odor similar to pennyroyal, was tested for oxidases and with positive results. The inflorescences gave the strongest reactions.

Calamintha nepeta yields an essential oil containing a large proportion of pulegone and menthone, but as it was not available the closely related species *Calamintha officinalis* Muh. was examined. The latter species smelled strongly of pulegone and gave positive results when examined for an oxidase. The strongest reactions were obtained with extracts of the inflorescences.

¹ Bull. Roure-Bertrand Fils, [1] 4, 18 (1901).

² Bruylants, Ber., 11, 449 (1878).

³ Wallach, Nachr. K. Ges. Wiss. Göttingen, 1, 11 (1901).

⁴ Ber., 43, 362 (1910).

Two distinctly negative results were obtained, which are interesting in that they are in harmony with the theory proposed. No reaction for an oxidase was obtained with aqueous extracts from two varieties of cultivated roses. German otto of rose contains a very small proportion of citral and a trace of nonyl aldehyde. The extracted oil may contain as much as 75 per cent. phenylethyl alcohol¹ but it is not known to contain phenylacetaldehyde or phenylacetic acid.

Negative results were also obtained with *Andropogon schoenanthus*, which yields palma rosa oil. This oil may contain as high as 93 per cent. of geraniol in addition to citronellol and dipentene. This is in marked contrast with the very closely related *Andropogon* grasses which yield lemon grass and citronella oils, both of which contain citral and citronellal as their major constituents. These species will be examined when the material is available.

The presence of an oxidase probably accounts for the fact that the perfumes of certain flowers deteriorate rapidly after picking, particularly if bruised, as is the case with champaca and gardenia flowers. The author ventures the opinion that flowers showing marked reactions for oxidases are not treated to the best advantage by the enfleurage method.

The action of oxidases from various sources on terpene alcohols will be taken up in the second paper on this subject.

GÖTTINGEN, GERMANY.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

CORRELATION OF IONIZATION AND STRUCTURE. II. NEGATIVELY SUBSTITUTED BENZOIC ACIDS.

By C. G. DERICK.

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1. Introduction.

In a previous article,² the author has shown that the free energy of ionization for negatively substituted monobasic paraffin acids in water solution at 25° is made up additively of the separate effects of each atom within the molecule. Because of this fact, it was shown that the position of a negative substituent in a paraffin acid could be determined with certainty if its α place factor and the ionization constant of this nega-

¹ v. Soden, *J. prakt. Chem.*, [2] 69, 265 (1904).

² THIS JOURNAL, 33, 1181 (1911).

tively substituted paraffin acid were known. The advantages of this method for the determination of structure over methods that use physical properties were pointed out. In the first place, no high degree of purity is necessary if the substituent is in the α , β , γ or δ positions, which is usually the case. A second advantage is due to the fact that no expensive apparatus and no exceptional skill are required to measure the ionization constant within the necessary limits. On the other hand, it was shown that in the calculation of the ionization constants from structure a much greater accuracy in the measurements of the ionization constants is required. Tables were given showing that the ionization constants for negatively substituted paraffin acids could be calculated with a degree of accuracy equal to that obtained in the measured values. This last fact constituted a rigid test of the statement that the free energy of ionization is made up additively of the separate influence of each atom in the molecule. Finally, it was shown that for the non-ionizing negative radicals, Cl, Br, I, OH and C_6H_5 , the place factors for the positions α , β , γ , δ , etc., possessed the following simple relationship α , $\alpha/3$, $\alpha/9$, $\alpha/27$, etc., respectively. It was also shown that even though a negative radical did not obey this "rule of thirds," its effect upon the free energy of ionization was still additive and from the experimentally determined place factors for the different positions of substitution, structures and ionization constants for such negatively substituted paraffin acids could be determined.

2. Place Factors for Negative Radicals in Aromatic Acids.

It is the purpose of this paper to show that the additive relationship in the free energy of ionization holds for the complex benzene derivatives of the aromatic series. It is therefore possible to determine the structure or ionization of negatively substituted benzoic acids if the ortho, meta and para place factors are known for each negative radical.

In the calculation of the place factors, the influence of all of the atoms in the molecule upon the ionization was defined as proportional to $1/\log K$, where K is the mass law constant. Hence this influence is inversely proportional to the free energy of ionization according to the expression $A = RT \log K$ where A is the free energy of ionization, for R and T (since all measurements are made at 25°) are constant. In order to determine the place factor for the given negative radical or atom in a given negatively substituted benzoic acid it becomes necessary to determine the effect of all the other atoms in this acid. This is accomplished as follows. In salicylic acid, the ortho hydroxyl place factor is desired. Leaving out of consideration this hydroxyl group, the other atoms in the molecule of salicylic acid differ from the corresponding unsubstituted benzoic acid, by a single hydrogen atom. The influence of all the atoms in benzoic acid is defined as proportional to $1/\log K$ and this may be

taken as the summation of the influences of the atoms in salicylic acid, excepting the influence of the ortho hydroxyl group, thereby neglecting the influence of a single hydrogen atom, which is justifiable, if it has a small value, since it occurs additively in the above. The ratio of the influence upon the ionization of the atoms in salicylic acid to the atoms in benzoic acid is then determined as follows:

$$\frac{\text{Salicylic}}{\text{Benzoic}} = \frac{1}{\text{Log K (salicylic)}} : \frac{1}{\text{Log K (benzoic)}} = \frac{-4.17457^1}{-2.98297} = \frac{1.399}{1}.$$

The influence of the ortho hydroxyl group upon the ionization or its *place factor* is therefore $1.399 - 1.000 = 0.3990$. The value for the ionization constant of benzoic acid is taken as 6.69×10^{-5} and is the average of three determinations reported by Lunden in his pamphlet, "Affinitätsmessungen an schwachen Säuren und Basen."

In Table I are given the ortho, meta, and para place factors for different negative radicals and atoms for benzoic acid, calculated in the same man-

TABLE I.—PLACE FACTORS OF THE NEGATIVE RADICALS IN MONOBASIC AROMATIC ACIDS.

Aromatic acid.			Radical.		
Name.	K _a .	Log K _a . ¹	Formula.	Position.	Place factor.
<i>o</i> -Acetohydroxybenzoic.	3.33×10^{-4}	-3.47756	CH ₃ CO ₂ —	<i>o</i>	0.200
<i>m</i> -Acetohydroxybenzoic.	9.9×10^{-5}	-4.00436	CH ₃ CO ₂ —	<i>m</i>	0.0425
<i>p</i> -Acetohydroxybenzoic.	4.2×10^{-5}	-4.37675	CH ₃ CO ₂ —	<i>p</i>	0.0462
Phthalaldehydic.	3.6×10^{-5}	-4.44370	HCO—	<i>o</i>	-0.0606
<i>o</i> -Benzoylbenzoic.	3.7×10^{-4}	-3.43180	C ₆ H ₅ CO—	<i>o</i>	+0.216
<i>o</i> -Bromobenzoic.	1.45×10^{-3}	-2.83863	Br—	<i>o</i>	0.471
Phthalic.	1.21×10^{-3}	-2.91721	CO ₂ H—	<i>o</i>	0.431
Isophthalic.	2.9×10^{-4}	-3.53760	CO ₂ H—	<i>m</i>	0.180
Terephthalic.	1.5×10^{-4}	-3.82391	CO ₂ H—	<i>p</i>	0.092
Methyl phthalate.	6.56×10^{-4}	-3.18310	CO ₂ CH ₃ —	<i>o</i>	0.311
Ethyl phthalate.	5.51×10^{-4}	-3.25885	CO ₂ C ₂ H ₅	<i>o</i>	0.281
<i>o</i> -Chlorobenzoic.	1.32×10^{-3}	-2.87943	Cl—	<i>o</i>	0.450
<i>m</i> -Chlorobenzoic.	1.55×10^{-3}	-2.80967	Cl—	<i>m</i>	0.486
<i>p</i> -Chlorobenzoic.	9.3×10^{-5}	-4.03156	Cl—	<i>p</i>	0.0355
<i>m</i> -Cyanobenzoic.	1.99×10^{-4}	-3.70115	CN—	<i>m</i>	0.128
<i>m</i> -Fluorobenzoic.	1.4×10^{-4}	-3.85387	F—	<i>m</i>	0.0832
* <i>o</i> -Hydroxybenzoic.	1.04×10^{-3}	-2.98297	(OH)—	<i>o</i>	0.399
<i>m</i> -Hydroxybenzoic.	1.04×10^{-3}	-4.07935	(OH)—	<i>m</i>	0.0233
<i>p</i> -Hydroxybenzoic.	2.9×10^{-5}	-4.53760	(OH)—	<i>p</i>	-0.0800
<i>o</i> -Iodobenzoic.	1.37×10^{-3}	-2.86328	I—	<i>o</i>	0.458
<i>m</i> -Iodobenzoic.	1.6×10^{-4}	-3.79588	I—	<i>m</i>	0.0997
Methylsalicylic.	8.1×10^{-5}	-4.09151	CH ₃ O—	<i>o</i>	0.0204
* <i>o</i> -Nitrobenzoic.	6.3×10^{-3}	-2.20066	NO ₂ —	<i>o</i>	0.897
* <i>m</i> -Nitrobenzoic.	3.44×10^{-4}	-3.46344	NO ₂ —	<i>m</i>	0.205
<i>p</i> -Nitrobenzoic.	4.0×10^{-4}	-3.39794	NO ₂ —	<i>p</i>	0.229
<i>o</i> -Methylolbenzoic.	1.5×10^{-4}	-3.82391	CH ₂ OH—	<i>o</i>	0.0917

¹ Log K is expressed as a negative logarithm.

* Acids so marked have been measured by two or more investigators.

ner as illustrated with the ortho hydroxyl place factor. The data are taken from Lunden's work just referred to. From the experimental study now in progress in this laboratory it is evident that in most cases the third figure in these place factors is doubtful, but no final word can be said on this point until a thorough study of the field has been completed.

3. Calculated Ionization Constants of Substituted Benzoic Acids.

From the place factors, given in Table I, the calculated ionization constants for the substituted benzoic acids, given in Table II, were computed. The method of calculation is the reverse of that just given under "Place Factors for Negative Radicals in Aromatic Acids." From the algebraic sum of the place factors representing the substituents in the acid whose ionization constant is desired, the above ratio of substituted benzoic acid to benzoic acid is determined and solved for the negative logarithm of the desired ionization constant, from which the algebraic value of the constant is determined.

In all the acids, the calculated and experimental value for the ionization constant fall within the same order. In twelve out of the twenty acids considered, the first significant figure in the calculated and experimental values are identical. It is very doubtful if the experimental results are known with an accuracy beyond this figure in the majority of cases, as will be shown in the experimental study of these place factors. In the cases where the experimental ionization constants have been measured by two or more investigators, the agreement with the calculated values is much closer. Such acids have been marked by an asterisk in Table II, from which we find the difference between the experimental and calculated values to be 7.4%, 1.7%, 33%, 12% and 9.9%. In all but one of the cases, the difference is well within the experimental error and the additive relationship of the place factors seems to be clearly established. On the other hand, the place factors representing a single hydrogen must be very small, since it was neglected in the calculation of the place factors for other radicals. However, the final word can be said only after a careful experimental determination of the above place factors.

4. Determination of Structure of Substituted Benzoic Acids from their Ionization Constants by Means of Place Factors.

The problem of determining the structures of negatively substituted acids from their ionization constants is much more complex than in the corresponding substituted paraffin acids. In the first place the rule of thirds does not apply, nor is there any apparent simple relationship between the place factors for a given group for the ortho, meta and para position. Hence the experimental ortho, meta and para place factors for each negative radical must be determined. These values, once ac-

TABLE II.—CALCULATED IONIZATION CONSTANTS OF POLYSUBSTITUTED BENZOIC ACIDS.

Name.	Aromatic acid.	Substituent.	Ionization constant.	
			Calculated.	Measured.
<i>o</i> -Chloro- <i>m</i> -nitrobenzoic.....		<i>o</i> -Cl, <i>m</i> -NO ₂ —	3.0 × 10 ⁻³	6 × 10 ⁻³
<i>m</i> -Chloro- <i>o</i> -nitrobenzoic.....		<i>m</i> -Cl, <i>o</i> -NO ₂ —	1.7 × 10 ⁻³	1.5 × 10 ⁻³
<i>p</i> -Chloro- <i>m</i> -nitrobenzoic.....		<i>p</i> -Cl, <i>m</i> -NO ₂ —	4.3 × 10 ⁻⁴	4.6 × 10 ⁻⁴
<i>p</i> -Chloro- <i>o</i> -nitrobenzoic.....		<i>p</i> -Cl, <i>o</i> -NO ₂ —	7.0 × 10 ⁻³	1.0 × 10 ⁻³
α -Methyl 3,6-dichlorophthalate.....		<i>m</i> -Cl, <i>o</i> -Cl, <i>o</i> -COOCH ₃	1.3 × 10 ⁻³	1.5 × 10 ⁻³
*2,5-Dihydroxybenzoic.....		<i>o</i> -(OH), <i>m</i> -(OH)	1.16 × 10 ⁻³	1.08 × 10 ⁻³
*2,3-Dihydroxybenzoic.....		<i>o</i> -(OH), <i>m</i> -(OH)	1.16 × 10 ⁻³	1.14 × 10 ⁻³
*2,4-Dihydroxybenzoic.....		<i>o</i> -(OH), <i>p</i> -(OH)	6.8 × 10 ⁻⁴	5.1 × 10 ⁻⁴
*3,4-Dihydroxybenzoic.....		<i>m</i> -(OH), <i>p</i> -(OH)	3.7 × 10 ⁻³	3.3 × 10 ⁻³
*3,5-Dihydroxybenzoic.....		<i>m</i> -(OH), <i>m</i> -(OH)	1.0 × 10 ⁻⁴	9.1 × 10 ⁻⁵
2-Methyl 4-hydroxyphthalate.....		<i>p</i> -(OH), <i>m</i> -(CO ₂ CH ₃)	4.0 × 10 ⁻⁴	2.0 × 10 ⁻⁴
Pyrogallol carboxylic (1 : 2 : 3 : 4).....		<i>o</i> -(OH), <i>m</i> -(OH), <i>p</i> -(OH)	7.7 × 10 ⁻⁴	5.5 × 10 ⁻⁴
5-Nitro-2-aldehydobenzoic.....		<i>o</i> -(HCO), <i>m</i> -(NO ₂)	2.2 × 10 ⁻⁴	1.0 × 10 ⁻⁴
1-Ethyl 4-nitrophthalate.....		<i>m</i> -(NO ₂), <i>o</i> -(CO ₂ C ₂ H ₅)	1.5 × 10 ⁻³	3.0 × 10 ⁻³
2-Ethyl 4-nitrophthalate.....		<i>p</i> -(NO ₂), <i>o</i> -(CO ₂ C ₂ H ₅)	1.7 × 10 ⁻³	5.2 × 10 ⁻³
1-Methyl 3-nitrophthalate.....		<i>o</i> -NO ₂ , <i>o</i> -(CO ₂ CH ₃)	1.3 × 10 ⁻³	1.6 × 10 ⁻³
2-Methyl 3-nitrophthalate.....		<i>m</i> -NO ₂ , <i>o</i> -(CO ₂ CH ₃)	1.8 × 10 ⁻³	2.1 × 10 ⁻³
<i>o</i> -Nitrosalicylic.....		<i>o</i> -(OH), (NO ₂)	1.52 × 10 ⁻³	1.57 × 10 ⁻³
<i>p</i> -Nitrosalicylic.....		<i>o</i> -(OH), <i>p</i> -(Cl)	2.7 × 10 ⁻³	8.9 × 10 ⁻³
<i>m,m</i> -Dinitrobenzoic.....		<i>m</i> -(NO ₂), <i>m</i> -(NO ₂)	1.1 × 10 ⁻³	1.6 × 10 ⁻³

*Acids so marked have been measured by two or more investigators.

curately determined, make it possible to calculate from the ionization constant, the structure of polysubstituted benzoic acids, where the substituent is a negative radical. The method will be illustrated as follows: A polyhydroxy benzoic acid has been prepared and its ionization constant has been measured. From its molecular weight and reaction with acetyl chloride, two hydroxyl groups are known to be present. We are, therefore, dealing with a dihydroxybenzoic acid. Theoretically, the following six are possible: $\text{CO}_2\text{H} : \text{OH} : \text{OH} = 1 : 2 : 3; 1 : 2 : 4; 1 : 2 : 5; 1 : 2 : 6; 1 : 3 : 4; 1 : 3 : 5$.

The algebraic sum of the place factors, corresponding to the hydroxyl group in each of the possible dihydroxybenzoic acids above, are, from Table I, respectively:

(1)	(2)	(3)
$o\text{-(OH)} = 0.399$	$o\text{-(OH)} = 0.399$	$o\text{-(OH)} = 0.399$
$m\text{-(OH)} = 0.023$	$p\text{-(OH)} = -0.080$	$m\text{-(OH)} = 0.023$
<hr/>	<hr/>	<hr/>
$o + m = 0.422$	$o + p = 0.319$	$o + m = 0.422$
(4)	(5)	(6)
$o\text{-(OH)} = 0.399$	$m\text{-(OH)} = 0.023$	$m\text{-(OH)} = 0.023$
$o\text{-(OH)} = 0.399$	$p\text{-(OH)} = -0.080$	$m\text{-(OH)} = 0.023$
<hr/>	<hr/>	<hr/>
$o + o\text{-(OH)} = 0.798$	$m + p = -0.057$	$m + m\text{-(OH)} = 0.046$

The ionization constant of the unknown dihydroxybenzoic acid is found to be 3.3×10^{-5} , from which the experimental place factor, representing the algebraic sum of the place factors for the two hydroxyl groups, is calculated to be -0.068 . Obviously the hydroxyl groups must be in the meta and para position and the unknown acid is 3,4-dihydroxybenzoic acid, since the only combination of two place factors for two hydroxyl groups whose algebraic sum will give the experimental value, -0.068 , is that represented by acid (5) above.

It is interesting to note that the para hydroxyl group behaves like a positive radical, decreasing the hydrogen ionization and therefore having a negative place factor in this consideration.

In the formation of new poly-substituted benzoic acids, this method for the determination of structure may be used very effectively to determine whether or not a molecular rearrangement has occurred within the molecule as well as to assign structure.

5. Limitations in the Use of Place Factors for the Determination of Structure in the Aromatic Series.

If the place factor for a given group in the ortho, meta or para position differ but little, it will be difficult to assign the structure for a given aromatic acid unless extreme accuracy in the measurement of the ionization constant is possible for the given acid. A study of Table I shows,

however, that this difficulty is not likely to interfere, seriously, in the majority of cases.

A far greater difficulty is presented by the fundamental conception of this work, namely, that the factor, representing the influence upon the ionization of all the atoms in the molecule (inversely proportional to the free energy of ionization), is made up *additively* of the separate influences of each atom. This means that each atom or radical exerts its influence upon the ionization independent of the other atoms or radicals and that the influence upon the ionization from a carboxyl group of a given radical will always be the same if it is the same distance from the ionizing group. For example, in 2,3- and 2,5-dihydroxybenzoic acids, the two hydroxyl groups are ortho and meta to the carboxyl group in both acids. This means, if the above additive relationship in the place factors is correct, that each should have the same ionization constant, since in each acid the hydroxyl groups are the same distance from the ionizing carboxyl group according to the hexagon formula for benzene. Experimentally the ionization constants for 2,3- and 2,5-dihydroxybenzoic acids are 1.06×10^{-3} and 1.14×10^{-3} , respectively. In other words, the substituent in position 3 will exert the same influence as in position 5 upon the carboxyl group in position 1 independent of the substituent in position 2 or 6. This fact is a peculiarity of the meta position for disubstituted benzoic acids. It is supported by many calculations in Table II where the value of the place factor of a given group is taken for the ortho, meta or para positions without regard to the other substituents in the molecule.

But Kekulé's "Atomic Linking Theory" predicts a difference between the 2,3- and 2,5-dihydroxybenzoic acids and this difference has been proven experimentally. Obviously, if the additive relationship in the place factor is true, as the above work has shown it to be, then the difference between the two acids is one of space relationship, since the relative distances between the groups in the 2,3- and the 2,5-dihydroxybenzoic acids must be the same. Ionization cannot, therefore, be used to determine this difference in structure, *i. e.*, it will not distinguish between the 3- and 5-positions in disubstituted benzoic acids, as it does not between the same positions in the mono-substituted benzoic acids.

6. A New Proof of the Equivalence of the Positions 3 and 5 with Respect to Position 1 in the Benzene Ring.

Hübner and Peterman¹ first proved that for a given position in the benzene ring there are two pairs of positions which with respect to this given position are equivalent. They observed "that ordinary bromobenzoic acid gives, on nitration, two isomeric nitrobromobenzoic acids. The latter, on reduction, yield the same aminobenzoic acid, *i. e.*, anthranilic

¹ *Ann.*, 149, 129 (1869). Also Cohen's "Organic Chemistry for Advanced Students," pages 438-444.

acid, which is related to salicylic acid." In other words in the pair 2-6, the positions 2 and 6 in the benzene ring with respect to 1 are equivalent. Later Noelting proved the same fact, as have numerous other investigators. These proofs have all been based upon the assumption that no molecular rearrangement occurs after the new radical has entered the molecule.

The additive relationship in the place factors for the negative substituents in substituted benzoic acids offers us a new proof of the symmetry of the benzene molecule. It offers us a means of detecting whether or not a molecular rearrangement follows the introduction of a new radical into the molecule.

In the previous section, it was shown that the positions 3 and 5 with respect to the position 1 in the benzene molecule are equivalent, independent of the substituents in the positions 2 and 6. This may be taken as a new proof of the equivalency of the pair of positions 3 and 5 with respect to position 1. But fortunately another proof is possible; for if we substitute a given radical into position 3 and the same radical into position 5, the algebraic sum of the place factors for these two positions must be just twice that for the single group in the meta position. For example, the place factor for the hydroxyl group in the meta position, taken from Table I, is equal to 0.023. The algebraic sum of the place factors for the two hydroxy groups in 3,5-dihydroxybenzoic acid, if the positions 3 and 5 are equivalent with respect to 1, is $2 \times 0.023 = 0.046$ from which we obtain the calculated ionization constant 1.0×10^{-4} . The experimental ionization constant for this acid is 9.1×10^{-5} and agrees with the calculated value within 10%, which is within the experimental error. Similarly the calculated value for the ionization constant of *m,m*-dinitrobenzoic acid, calculated on the assumption of the equivalency of positions 3 and 5 with respect to 1, is 1.1×10^{-3} , while the experimental value is 1.6×10^{-3} . These two examples, as well as the acids mentioned under the previous sections, prove clearly that the positions 3 and 5 with respect to position 1 in the benzene ring are equivalent from an energy standpoint, since the place factor is inversely proportional to the free energy of ionization.

7. Summary.

(1) The place factors for benzoic acid for the radicals acetohydroxy carboxyl, chlorine, hydroxyl, and nitro, for the ortho, meta and para positions; aldehyde, benzoyl, bromine, carboxymethyl, carboxyethyl iodine and methoxy for the ortho position; and cyanogen, fluorine and iodine for the meta position have been determined.

(2) No simple relationship exists between the ortho, meta, and para place factors for the same radical substituted in benzoic acid.

(3) The calculated ionization constants for twenty polysubstituted

benzoic acids have been compared with their experimental ionization constants and found to agree fairly accurately in all but four cases. For those acids whose ionization constants have been measured by two or more investigators, the agreement between the calculated and experimental values is within the limit of the experimental error in all but one acid.

(4) A method for the determination of the structure of polysubstituted benzoic acids from their ionization has been developed.

(5) Ionization will not distinguish the difference in structure of 2,3- and 2,5-disubstituted benzoic acids where the substituents in 3 and 5 are the same and the substituent in 2 is also the same in both acids.

(6) The equivalency of the positions 3 and 5 with respect to position 1 in the benzene ring has been proven in terms of the free energy of ionization.

(7) The assumption that the free energy of ionization is made up additively of the separate influence of each atom in the molecule of an acid has received further substantiation.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE FORMATION OF PYRIMIDINES BY USE OF NITROMALONIC ALDEHYDE.¹

BY WILLIAM J. HALE AND HARVEY C. BRILL.

Received November 7, 1911.

When either acetone or one of its mono- or symmetrical di-substitution products is allowed to act upon nitromalonic aldehyde, a condensation readily takes place. The course of these condensations was thoroughly investigated by Hill and his coworkers.² In all of the cases studied, the acetone nucleus was involved with the two aldehyde groups conjointly, and resulted in the formation of six-membered ring compounds—derivatives of benzene. Derivatives of acetone higher than the symmetrical di-substitution products could not be made to enter into the reaction. There arose, therefore, the necessity of explaining these results through the formation of an intermediate product—a derivative of dihydrobenzene. This latter, by the elimination of water, readily underwent a transformation to the benzene type. Two free hydrogen atoms upon either end of the acetone nucleus are thus shown to be a prerequisite for this condensation with nitromalonic aldehyde.

Substances possessing amino groups, and thereby two free hydrogen

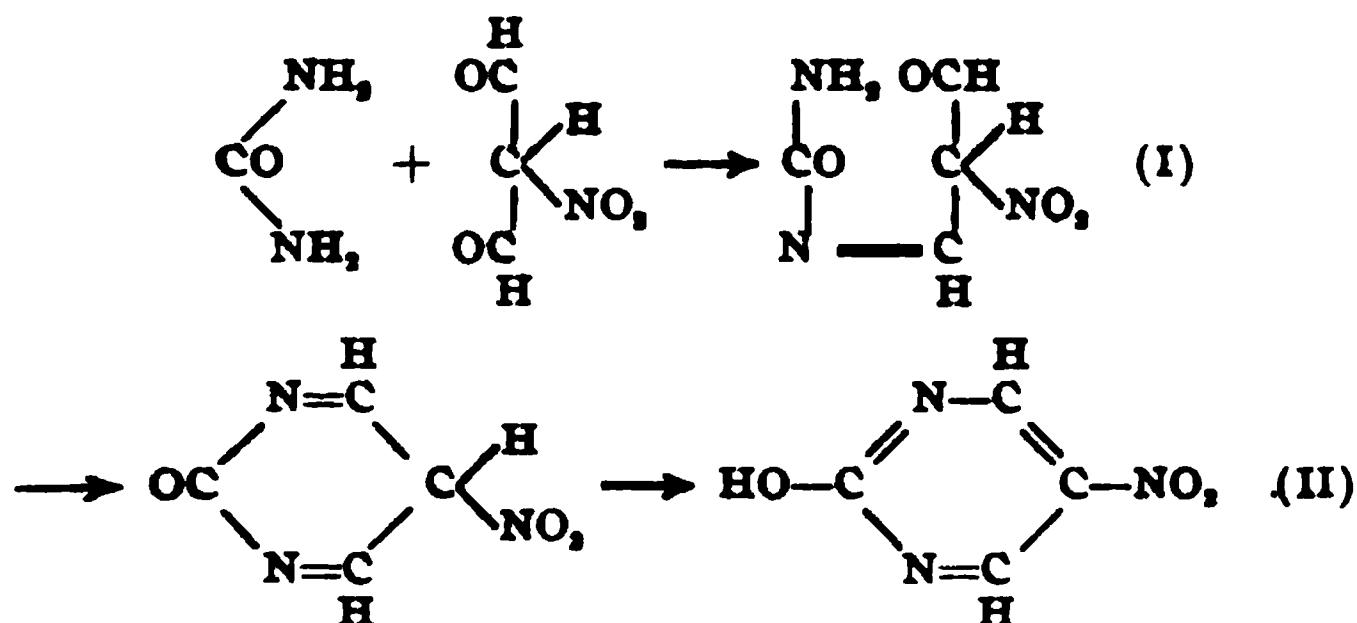
¹ The work described in this article formed part of a thesis presented to the Faculty of the Department of Literature, Science and the Arts of the University of Michigan for the degree of Doctor of Philosophy, by Harvey C. Brill.

² *Am. Chem. J.*, 22, 89 (1899); 24, 1 (1900); 33, 1 (1905).

atoms attached to a nitrogen atom, were found very reactive toward nitromalonic aldehyde, but beyond the monoamino derivatives Hill and his coworkers did not proceed.

From the facts thus stated and from the ideas so freely presented to one of us by Professor Hill himself, we determined to investigate this action of nitromalonic aldehyde upon the α -diamino compounds. If analogy might hold, then, urea, the simplest member of that class of α -diamino compounds possessing a carbonyl group in the same relative position as in acetone, should condense with this aldehyde to give a six-membered ring containing two nitrogen atoms in the meta position—namely, a pyrimidine. Pinner¹ has accomplished the synthesis of pyrimidines by making use of various amidines with β -diketones or ketonic esters; in all cases the reactions ran quite smoothly and with good yields.

The reaction of nitromalonic aldehyde with urea is best accomplished in aqueous solution. Sodium hydroxide was used as a condensing agent just as in the work upon acetone derivatives already cited. The results, however, were often bettered by use of piperidine in this same capacity. The solutions soon acquired a yellow color and later developed a deep red. Upon acidification a semi-crystalline, faintly yellow precipitate appeared in fair quantity, and later, upon standing, the mother liquors yielded a yellow leaf-like precipitate in much smaller quantity. The first product (I) melted at 154° (cor.) and proved to be a monoureide of nitromalonic aldehyde. The second product (II) melting at 203.5° (cor.) was shown to be the pyrimidine anticipated. We may represent the reaction as follows:

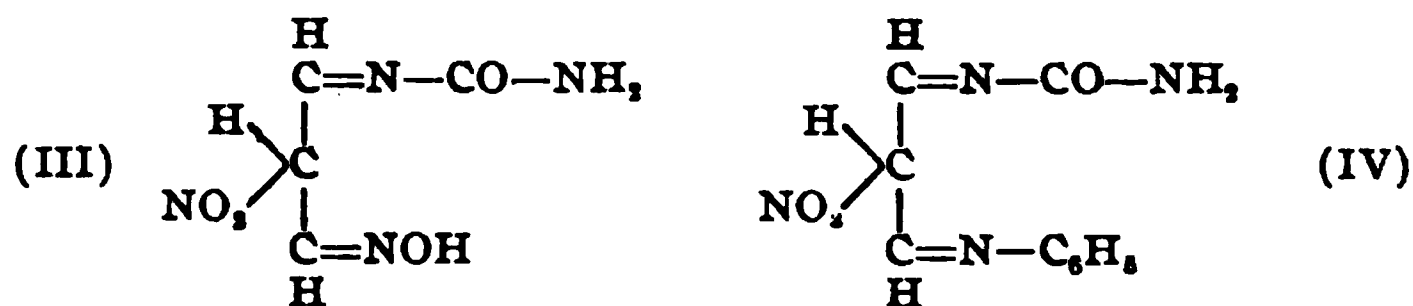


The monoureide is a much less stable compound than the pyrimidine. It contains, as the formula indicates, a free aldehyde group readily recognizable by characteristic reactions. The monoxime (III) may easily be prepared, but the monanil (IV) offered considerable difficulty. The action of aniline upon the monoureide had a tendency to replace the urea nucleus itself and form at once the monanil of nitromalonic aldehyde²

¹ *Ber.*, 23, 161 (1890); 26, 2125 (1893).

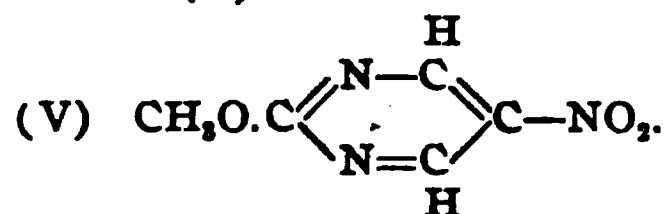
² *Am. Chem. J.*, 22, 99 (1899).

together with free urea. In order to effect this combination it was necessary first to prepare the nitromalonic aldehyde monanil and suspend this



in alcohol containing the theoretical amount of urea (1 mol.). Into this solution was passed a current of dry hydrogen chloride. After standing, the long slender red needles of nitromalonic monoureide anil made their appearance. Similar attempts to prepare a phenylhydrazone of this monoureide were unsuccessful. Phenylhydrazine replaces the urea nucleus and leads at once to the 1-phenyl-4-nitropyrazole.¹ Several salts of the monoureide were made and analyzed.

It is evident that the monoureide is only an intermediate step in the formation of a dihydropyrimidine, and that this immediately passes over into a pyrimidine by the loss of one molecule of water. This transformation runs poorly at best, but is favored by the presence of a dehydrating agent such as is the excess of sulfuric acid added to the original reaction-mixture. Hydrochloric acid is not as effective. The slight solubility of this monoureide in the acidified mother liquor offers only small chance for any appreciable formation of pyrimidine. The yield of pyrimidine, however, may be substantially increased by warming the original reaction-mixture to about 40° before acidification. Again, the monoureide when dissolved in acetic anhydride and warmed either alone, or with the presence of sulfuric acid, or anhydrous hydrogen chloride, underwent a partial transformation into the pyrimidine. Attempts carried out under pressure were altogether disastrous. The most effective method for bringing about this further condensation consisted in the use of sodium ethylate upon the warm alcoholic solution of the monoureide. Acidification of the final mixture gave a fair yield of pyrimidine. The methyl ether of this pyrimidine was prepared and shown to have a constitution corresponding to a 5-nitro-2-methoxypyrimidine (V):



The probable formation of a dihydropyrimidine as the intermediate product in passing from the monoureide to the pyrimidine has a possible substantiation in the work of P. N. Evans² and A. and C. Combes.³

¹ *Am. Chem. J.*, 22, 105 (1899).

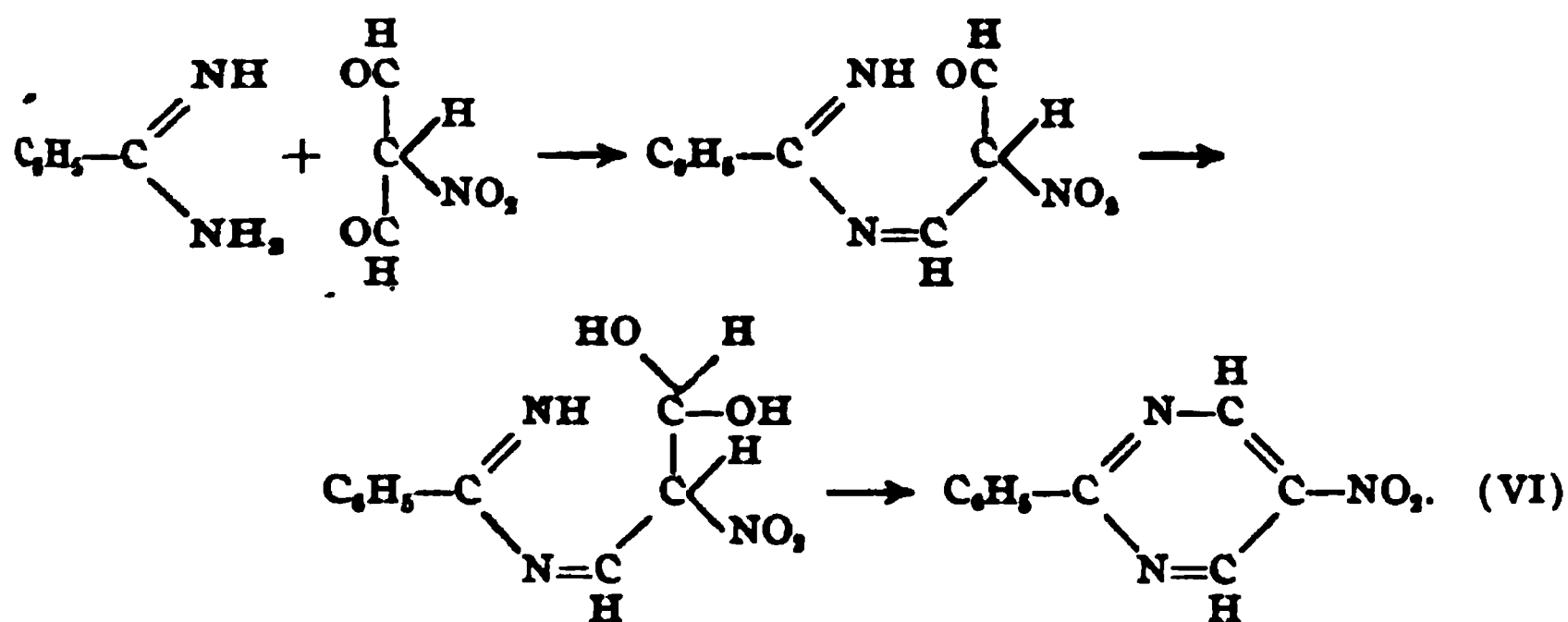
² *J. prakt. Chem.*, [2] 48, 489 (1893).

³ *Bull. soc. chim., Paris*, [3] 7, 788 (1892).

These investigators assumed a structure of such a type for the condensation product obtained from urea and acetylacetone.

This production of a pyrimidine by the action of urea upon nitromalonic aldehyde is attended, therefore, with difficulty and by only small yield. In marked contrast are the condensations carried out by Pinner between β -diketones and amidines. Accordingly, it seemed advisable to try the action of amidines upon nitromalonic aldehyde with a view to studying the influence and rôle which the imino group might play in these reactions.

Benzamidine in the form of its hydrochloride was introduced into an aqueous solution of sodium nitromalonic aldehyde. From this mixture a white crystallin precipitate was thrown down almost immediately, even without the presence of a condensing agent. The product, quantitative in yield, showed the presence of neither hydroxyl nor aldehyde group, but accorded through analyses with a true pyrimidine a 5-nitro-2-phenylpyrimidine (VI). The reaction must have proceeded in accordance with the following scheme:

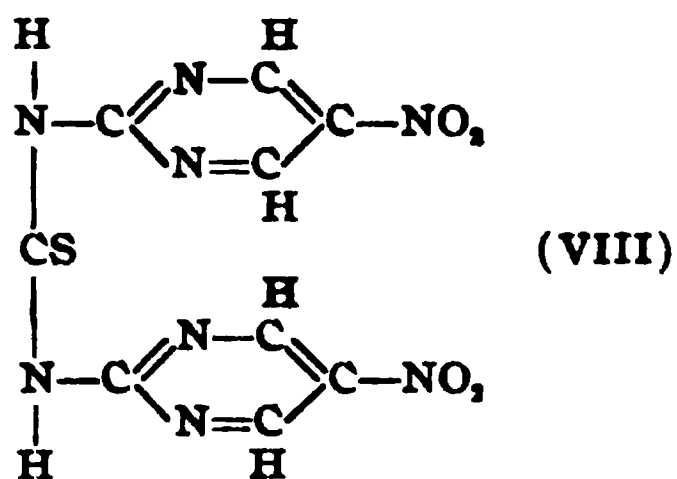
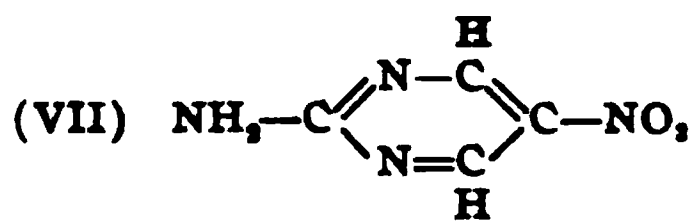


An intermediate compound, as represented above by the condensation between the amino group and one aldehyde group, is no doubt first formed; but the imino group almost immediately reacts with the second aldehyde group, in hydrated form, whereby two molecules of water are lost, the first in the ring closing and the second in the appearance of the unsaturated linkage. The constitution of the intermediate product is indeed most favorable for the second reaction. This tendency for the imino group to enter so readily into a condensation with the hydrated aldehyde group, leaving the second hydroxyl to split off with the hydrogen of the adjoining carbon atom, accounts most likely for the speed and facility with which this condensation is found to run.

The presence of one amino group and one imino group upon the same carbon atom of a compound seems therefore to be the most favorable grouping for the pyrimidine formation. That series of compounds known as the amidines presents exactly this arrangement and constitutes there-

fore the best possible basis for pyrimidine formation. No matter what other group may be associated with the amidine nucleus, $-C(:NH).(NH_2)$, this tendency to enter into condensation with β -ketonic derivatives should be apparent. From the study of urea it has already been noted with what difficulty the pyrimidine ring is formed when two amino groups in this same position are concerned. The presence therefore of a second amino group in conjunction with the amidine nucleus should not interfere with the ease by which the amidine grouping could enter into condensation. Such a compound is guanidine and by its use in this connection, we should ascertain at once the correctness of this view. With nitromalonic aldehyde guanidine should give a nitroaminopyrimidine. Otherwise, if the two amino groups enter preferably into the reaction, as may well be inferred from the study of urea, we should obtain a nitroiminopyrimidine.

Upon bringing guanidine and nitromalonic aldehyde together, in an aqueous solution, the solution took on a red color at once and a colorless, needle-like, crystallin substance was precipitated—even without a condensing agent. The yield, however, may be made quantitative by use of piperidine as the condensing agent. The product thus obtained gave an affirmative test for the presence of an amino group (carbylamine reaction) and a negative test for the presence of an imino group (Liebermann's nitrosamine reaction). From these and other tests no question remains but that the product contains only the amino group, and this in the 2-position in the pyrimidine ring. Analysis accorded with the formula (VII) a 5-nitro-2-aminopyrimidine.



Attempts to prepare the hydrochloride of this nitroaminopyrimidine were unsuccessful. This failure is no doubt due to the strongly negative nature of the nitropyrimidine, and again to the resistance afforded to any substituent upon a carbon atom of a ring situated between two nitrogen atoms. There is, therefore, no tendency for an aminic nitrogen in such position to become basic. On the other hand, an acyl derivative of the amino group is possible, as shown by the preparation of a monoacetylaminopyrimidine by the action of acetic anhydride upon the aminopyrimidine.

When this aminopyrimidine is warmed in carbon disulfide with the

presence of a small amount of alkali, a yellow, oily mass is precipitated. This, upon digestion in alcohol, soon solidifies to a yellow crystallin compound—a characteristic property of this compounds. Analysis showed the substance to be a 5,5'-dinitro-2,2'-dipyrimidylthiocarbamide (VIII).

Hot dilute alkali dissolves the 5-nitro-2-aminopyrimidine but does not attack it. When boiled, however, with a highly concentrated alkaline solution, this pyrimidine is slowly attacked and ammonia set free from the deep red mixture. The solution then contains the 5-nitro-2-hydroxypyrimidine, which can be precipitated out in the form of its silver salt. The free hydroxypyrimidine obtained from the silver salt is in all respects identical with the hydroxypyrimidine procured by the action of urea upon nitromalonic aldehyde. This hydrolysis proves conclusively that the amino group in the pyrimidine must occupy the same relative position as the hydroxyl group in the product from urea, i. e., the 5-nitro-2-hydroxypyrimidine.

The condensation of urea with nitromalonic aldehyde has proceeded only through the formation of a monoureide. An excess of urea seemed in no way to favor the possible formation of a diureide. In order to change the conditions as much as possible it was decided to employ also certain monoalkyl- or arylureas. Such, for example, as methylurea, benzylurea, or phenylurea. In all of these cases only the monoalkyl- or arylureide of nitromalonic aldehyde was procured. The reaction with benzylurea has appeared somewhat more rapid than with the others.

The presence in these substituted ureas of a secondary nitrogen might also have indicated the possibility of a ring formation involving the free aldehyde group of the alkylated monoureide, in similar manner to that displayed by the imino groups of the amidines. As no compounds of the pyrimidine class were obtained, there remains only the conclusion that it is the imino group itself and not a secondary nitrogen atom which serves so well under these conditions for the pyrimidine ring synthesis.

Experimental Part.

Nitromalonic Aldehyde Monoureide, $C_5H_5NO_5(:N.CO.NH_2)$ (I).—Equimolecular quantities of urea (1.2 grams) and sodium nitromalonic aldehyde (3 grams) were brought together in aqueous solution (30 cc.), and a few drops of piperidine added as condensing agent. Two or 3 cc. of N sodium hydroxide solution serve here equally as well. After 24–36 hours the deep red reaction mixture was acidified with dilute sulfuric acid, upon which a light yellow crystallin precipitate immediately formed. Upon filtering off this monoureide, 1 gram in weight, the mother liquor yielded, in the course of 48 hours or more, 0.2 gram of a second precipitate somewhat more granular and less crystallin than the first. This product is the pyrimidine.

The monoureide thus obtained, and purified by crystallization from alcohol, melted at 154° (cor.). It is readily soluble in alcohol, acetic ester or acetic acid; only fairly soluble in acetone or water; and insoluble in chloroform, ether, benzene, carbon disulfide or carbon tetrachloride. It slowly undergoes decomposition and cannot therefore be preserved for any length of time.

Calculated for $C_4H_5N_3O_4$: C, 30.20; H, 3.17; N, 26.46

Found: C, 30.40; H, 3.40; N, 26.82

Sodium Salt of Nitromalonic Aldehyde Monoureide.—The sodium salt was easily prepared by adding sodium ethylate to an alcoholic solution of the monoureide. The salt is deposited as a light brown precipitate, slightly soluble in alcohol, but readily soluble in water. It decomposes violently upon warming. The salt analyzed was purified by crystallization from dilute alcohol. All of its water of crystallization is lost over sulfuric acid.

Calculated for $NaC_4H_4N_3O_4 \cdot 3H_2O$: H_2O , 22.97; Na, 9.77

Found: H_2O , 22.84, 23.87; Na, 10.86, 9.61

Nitromalonic Aldehyde Ureide-Anil, $C_9H_8NO_2(:N.C_6H_5)(:N.CO.NH_2)$ (IV).—When the monoureide and aniline, in equimolecular quantities, were brought together in a warm alcoholic solution, nitromalonic aldehyde monanil, m. p. 144° , was formed.¹ The ureide group is thus seen to be readily displaceable by aniline. If, however, equimolecular quantities of nitromalonic aldehyde monanil and urea are dissolved in alcohol and a current of dry hydrogen chloride led into the solution till saturation is reached, there appears, upon cooling, a precipitate of glistening, red, needle-like crystals. This substance is the ureide-anil, easily purified by crystallization from alcohol and melting at 211° (cor.). This ureide-anil is readily soluble in chloroform, acetone or benzene; slightly soluble in alcohol, carbon tetrachloride, water or acetic ester; and insoluble in ether or ligroin.

0.1752 gram of substance gave 0.3260 gram CO_2 and 0.0720 gram H_2O .

Calculated for $C_{10}H_{10}N_4O_3$: C, 51.26; H, 4.30

Found: C, 51.93; H, 4.70

Nitromalonic Aldehyde Ureide-Oxime, $C_3H_3NO_2(:NOH)(:N.CO.NH_2)$ (III).—The monoureide was introduced into a solution containing the calculated amount of hydroxylamine hydrochloride (1 mol.) and just sufficient alkali added for neutralization. A yellow leaf-like crystalline precipitate appeared on short standing. This product is the monoureide-oxime. It is somewhat soluble in alcohol, acetone, acetic ester or acetic acid; insoluble in chloroform, ether, benzene or ligroin. When recrystallized from alcohol it melted at $174-5^{\circ}$ (cor.).

Calculated for $C_4H_5N_4O_4$: C, 27.58; H, 3.47

Found: C, 27.52; H, 4.11

¹ *Am. Chem. J.*, 22, 99 (1899).

Attempts to prepare the monoureide-phenylhydrazone were unsuccessful. In all cases urea was split off from the nitromalonic aldehyde monoureide and replaced by the phenylhydrazine radicle, whereby the 1-phenyl-4-nitropyrazole, as previously mentioned, was formed by intramolecular condensation.

The ease with which urea is eliminated from this nitromalonic aldehyde monoureide by means of aniline or phenylhydrazine made possible a simple determination of the urea per molecule of product. To an alcoholic solution of the monoureide the theoretical amount of aniline was added, and the solution then titrated against a solution of mercuric nitrate. In this method of Liebig the mercuric nitrate solution was made up so that 1 cc. was equivalent to 0.07 gram HgO and about equivalent to 0.01 gram urea.

Calculated for $C_4H_5N_3O_4$: 1 mol. urea 37.74%; found, 35.10%

5-Nitro-2-hydroxypyrimidine, $C_4H_3N_3O_4$ (II).—This product appears in the course of a few hours' standing of the mother liquor left after the removal of nitromalonic aldehyde monoureide previously described. The formation is continuous for two or three days, but only in very small quantities. It appears in small yellow plates, of a deeper color than the monoureide, and is insoluble in water, carbon disulfide, ether, chloroform, carbon tetrachloride, ligroin or benzene; sparingly soluble in acetone, acetic ester or alcohol and only slightly soluble in hot acetic acid or its anhydride. It may be recrystallized, but with difficulty, from glacial acetic acid; the m. p. is 203.5° (cor.).

Calculated for $C_4H_3N_3O_4$: C, 34.03; H, 2.14; N, 29.80

Found: C, 33.92; H, 2.40; N, 29.69

When 1.2 grams of sodium nitromalonic aldehyde and 0.3 gram urea were brought into reaction, the mother liquor, left after the removal of the monoureide within a few minutes after the acidification, scarcely ever yielded more than 0.2 gram pyrimidine, *i. e.*, 18% of the theoretical.

By far the larger portion of the product in this reaction consists of the monoureide, from 70–80% of theoretical yield. Experiments, therefore, which might lead to a further condensation in the molecule of this ureide were extensively pursued. When the monoureide is dissolved in acetic anhydride and anhydrous hydrogen chloride led into the solution, there appeared upon cooling a small quantity of the pyrimidine, 10–15% of the theoretical yield. An excess of dilute sulfuric acid added to the reaction-mixture of nitromalonic aldehyde and urea suffices to increase the yield in pyrimidine, providing that the mixture is kept near 50° . On the other hand the action of dilute sulfuric acid upon the free monoureide in aqueous suspension, even when warmed, is not as effective. When heated in sealed tubes with acetic anhydride, either alone or in the presence of zinc chloride, anhydrous sodium acetate or phosphorus pent-

oxide, the monoureide underwent decomposition, whereas the use of similar agents in the same solvent at room temperature was ineffective altogether.

Sodium Salt of 5-Nitro-2-hydroxypyrimidine.—The sodium salt of this pyrimidine may be prepared in fair yield by warming an alcoholic solution of the monoureide with excess of sodium ethylate over a water bath for several hours. The sodium salt of the pyrimidine is less soluble in alcohol than that of the monoureide, consequently it is found to separate out almost as fast as formed. This sodium salt was obtained in 10–15% yield. When recrystallized from water the red crystals accorded with the following analyses:

Calculated for $\text{NaC}_4\text{H}_3\text{N}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$: H_2O , 18.59; Na, 11.56

Found: H_2O , 17.82; Na, 12.38

Potassium Salt of 5-Nitro-2-hydroxypyrimidine.—In a similar manner to that for the preparation of the sodium salt, the potassium salt may be obtained by use of potassium ethylate. Or, if desired, potassium hydroxide may be used to dissolve the free pyrimidine and the neutral deep red solution evaporated to the point of crystallization, when the yellow prismatic crystals of the potassium salt come out.

Calculated for $\text{KC}_4\text{H}_3\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$: H_2O , 9.14; K, 19.80

Found: H_2O , 8.99; K, 19.60

Barium Salt of 5-Nitro-2-hydroxypyrimidine.—When the pyrimidine is dissolved in ammonium hydroxide and barium hydroxide added to this neutral solution, a reddish brown precipitate of the barium salt is thrown down. This salt lost all of its water of crystallization at 110° .

Calculated for $\text{BaC}_4\text{H}_3\text{N}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$: H_2O , 14.73; Ba, 24.08

Found: H_2O , 13.30; Ba, 24.04

Silver Salt of 5-Nitro-2-hydroxypyrimidine.—The silver salt was prepared by adding a solution of silver nitrate to one of the ammonium salt of the pyrimidine. It is of a reddish yellow color and only slightly soluble in water.

Calculated for $\text{AgC}_4\text{H}_3\text{N}_2\text{O}_3$: Ag, 43.55; found, 43.10

5-Nitro-2-methoxypyrimidine, $\text{C}_4\text{H}_3\text{N}_2(\text{NO}_2)(\text{OCH}_3)$ (V).—The dried sodium salt of the hydroxypyrimidine, suspended in absolute alcohol, was warmed with methyl iodide, under reflux condenser, for two or three hours. The mixture was then evaporated to dryness over a water bath and the residue extracted with benzene. The yield is very poor. After several recrystallizations from benzene the pure product melted at $168-9^\circ$ (cor.). Upon repeated melting and recooling the ether always gave this same melting point, indicating therefore no tendency for transformation or wandering of the methoxyl group. It is a colorless, plate-like crystalline substance, readily soluble in benzene; fairly soluble in alcohol, but insoluble in ether.

Calculated for $C_8H_8N_2O_3$: C, 38.69; H, 3.25

Found: C, 38.86; H, 3.49

A determination of the position of the methoxyl group in this ether was carried out in accordance with the method of Zeisel. The ether was placed in a small flask, containing also a solution of hydriodic acid and ammonium iodide and warmed very gently. The methyl iodide evolved was led through a series of flasks containing hydriodic acid, water, and moist red phosphorus in order, and finally into one containing a diluted alcoholic solution of silver nitrate. A temperature of only 40° was found sufficient to decompose the ether and liberate all of the methyl iodide, which was to be determined as silver iodide in the last of the flasks, just mentioned. This low temperature (usually given as between 40° and 80° for such determinations) indicates that we have the methoxyl group attached to a carbon atom and not to a nitrogen in the pyrimidine ether.

Calculated for $C_8H_8N_2O_3$: CH_3 , 9.68%; found, 7.99%.

Many attempts were made toward effecting a reduction of the free nitrohydroxypyrimidine, but decomposition interfered in all cases.

5-Nitro-2-phenylpyrimidine, $C_8H_8N_2(NO_2).C_6H_5$ (VI).—Equimolecular quantities of benzamidine hydrochloride and sodium nitromalonic aldehyde, when brought together in aqueous solution, gave a white flocculent precipitate almost immediately. The presence of sodium hydroxide as a condensing agent was found to retard somewhat this precipitation, but by acidification the total yield (practically quantitative) could be realized. Consequently, the sodium salt of the intermediate product necessarily formed in this condensation must have undergone an immediate hydrolysis. The pyrimidine is fairly soluble in alcohol, ether, or benzene, but insoluble in water. The product was best purified by crystallization from an alcohol and ether solution. The soft white plates gave a melting point of 219° (cor.).

Calculated for $C_{14}H_{10}N_4O_3$: C, 60.00; H, 3.51; N, 20.89

Found: C, 60.17; H, 3.78; N, 20.82

5-Nitro-2-aminopyrimidine, $C_4H_4N_4(NO_2).(NH_2)$ (VII).—When equimolecular quantities of guanidine carbonate and sodium nitromalonic aldehyde were mixed in aqueous solution there appeared immediately a flocculent white precipitate. The yield was made almost quantitative by use of a few drops of piperidine as condensing agent. The product is soluble in alkali and reprecipitated by addition of acid. It is soluble in acetone, alcohol or acetic ester; fairly soluble in water; insoluble in ether, ligroin, chloroform, benzene or carbon tetrachloride. Recrystallized from alcohol, the fine, colorless needles melted at 236° (cor.).

Calculated for $C_4H_4N_4O_3$: C, 34.27; H, 2.87; N, 40.01

Found: C, 34.00; H, 2.59; N, 40.17

The presence of a free amino group in this pyrimidine was confirmed

by several qualitative tests, such, for example, as the "carbylamine" reaction with alcoholic potassium hydroxide. The Hinsberg test with benzene sulfochloride gave only a clear solution and no oily product as is obtained with compounds containing the imino group. Upon addition of sodium nitrite to an acid solution of this pyrimidine the absence of an oily product further confirmed the absence of an imino group (Liebermann).

When the aminopyrimidine is boiled with alkali, a rapid evolution of ammonia is detected. In fact ammonium hydroxide itself is sufficient for this hydrolysis. When a solution of the aminopyrimidine in concentrated ammonium hydroxide is boiled till no further odor of ammonia is noted, and silver nitrate then added to the deep red solution, there appeared a reddish brown precipitate of a silver salt which proved to be the silver salt of 5-nitro-2-hydroxypyrimidine.

Calculated for $\text{AgC}_4\text{H}_3\text{N}_3\text{O}_2$: N, 16.93; Ag, 43.55

Found: N, 16.60; Ag, 41.35, 43.36

This silver salt of the 5-nitro-2-hydroxypyrimidine, as prepared from the aminopyrimidine, was next heated in aqueous suspension with hydrochloric acid and the clear solution filtered from the silver chloride thus formed. Upon evaporation to small bulk, the light yellow, semicrystalline hydroxypyrimidine made its appearance, in all respects identical with the hydroxypyrimidine prepared from urea and nitromalonic aldehyde. By the action of methyl iodide upon this silver salt suspended in absolute methyl alcohol, at the temperature of a water bath, there was obtained, in like manner to the process already described, the same identical 5-nitro-2-methoxypyrimidine prepared by the action of methyl iodide upon the silver salt of the hydroxypyrimidine obtained from urea.

When the aminopyrimidine was warmed with a slight excess of an approximately normal sodium hydroxide solution, until the odor of ammonia was no longer apparent, and this deep red solution evaporated with much care upon a water bath, the reddish-brown crystals of the sodium salt of the hydroxypyrimidine came out. An analysis showed that the product contained two molecules of water of crystallization and was in all respects identical with the sodium salt of the hydroxypyrimidine previously described.

5-Nitro-2-acetylaminopyrimidine, $\text{C}_4\text{H}_3\text{N}_3(\text{NO}_2)(\text{NHCOCH}_3)$.—The acetyl derivative was obtained by warming the aminopyrimidine with an excess of acetic anhydride in presence of anhydrous sodium acetate. The solution was heated for a period of three hours upon the steam bath, after which, upon cooling, the acetyl compound crystallized out in beautiful, long, colorless needles. The yield amounted to 80% of the theoretical. The product is readily soluble in acetic acid, benzene, alcohol or chloroform; slightly soluble in water, carbon tetrachloride, acetic ester or acetone;

and insoluble in ether or ligroin. When purified by recrystallization from alcohol it melted at 172.5° (cor.).

Calculated for $C_8H_6N_4O_3$: N, 30.86; found, 30.84

Attempts to prepare the hydrochloride of the 5-nitro-2-aminopyrimidine were unsuccessful. Various acids were employed in this connection to ascertain what amino salt might be formed, but in no case could any action be detected. This amino group is thus shown to be very resistant.

5,5'-Dinitro-2,2'-dipyrimidyl Thiocarbamide (VIII), $CS(NH.(C_4H_3N_2NO_2))_2$.—When 5-nitro-2-aminopyrimidine was suspended in carbon disulfide and a small amount of potassium hydroxide added to this mixture, kept at 60° , a yellow, oily mass collected after a short time at the bottom of the vessel. Upon removal this product was digested with alcohol and soon passed over into a mass of glistening leaflets. This thio-compound is soluble in alcohol, carbon disulfide or acetic ester; fairly soluble in water or ether; slightly soluble in acetone, chloroform or benzene; insoluble in ligroin or carbon tetrachloride. Recrystallized from alcohol the pure product melted at $230-1^{\circ}$ (cor.). Attempts to liberate the aminopyrimidine from this thio-compound were unsuccessful. Decomposition took place in all cases.

Calculated for $C_8H_6N_4O_4S$: N, 34.78; found, 34.36

Nitromalonic Aldehyde Monophenylureide, $CHO.CH(NO_2)CH : N.CO.NH.C_6H_5$.—Equimolecular quantities of nitromalonic aldehyde and phenylurea were brought together in alcoholic solution and a few drops of piperidine added. Though a portion of the product is precipitated in a short time, the solution must be acidified to effect a complete separation of the free substance. This monophenylureide is soluble in alcohol or ether but insoluble in water. Recrystallized from alcohol it melted at $176-7^{\circ}$ (cor.).

Calculated for $C_{11}H_9N_3O_4$: C, 51.06; H, 3.86

Found: C, 49.80; H, 4.10

Nitromalonic Aldehyde Monobenzylureide, $CHO.CH(NO_2).CH : N.CO.NH.CH_2.C_6H_5$.—When benzylurea and nitromalonic aldehyde were brought together in alcoholic solution in the presence of a few drops of piperidine, a condensation took place almost immediately, as noted by the deepening in red color of the solution. Upon acidification the colorless leaflets of the free benzylureide were thrown down. This product is soluble in alcohol, chloroform, acetone or acetic ester; insoluble in benzene, carbon tetrachloride or ligroin. Recrystallized from alcohol it melted at $150-1^{\circ}$ (cor.).

Calculated for $C_{11}H_{11}N_3O_4$: N, 16.86; found, 16.18

Nitromalonic Aldehyde Monomethylureide, $CHO.CH(NO_2).CH : N.CO.NHCH_3$.—This product was prepared by bringing together monomethylurea and nitromalonic aldehyde in aqueous solution. After the addition

of a few drops of piperidine the color of the solution indicated the completion of the reaction in about one day. Upon acidification, the yellow crystals of the monomethylureide were precipitated. This product is soluble in alcohol or acetone; fairly soluble in chloroform, acetic ester or ligroin; insoluble in ether, benzene or carbon tetrachloride.

Calculated for $C_6H_7N_3O_4$: C, 34.64; H, 4.04

Found: C, 34.84; H, 3.88

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, SECTION OF AGRONOMY,
IOWA AGR. EXPT. STA.]

THE CHEMICAL NATURE OF THE ORGANIC NITROGEN IN THE SOIL.

[SECOND PAPER.]

BY S. L. JODIDI.

Received October 26, 1911.

By applying the Hausmann-Osborne¹ method, as well as the formaldehyde² titration method perfected by Sørensen, the writer³ has demonstrated that the acid-soluble organic nitrogen occurring in Iowa soils and in Michigan peat soils is made up chiefly of acid amides, monoamino acids and diamino acids. In the meantime, and in part before those publications, there appeared several papers dealing with the isolation of organic nitrogenous compounds from soils. Thus, Schreiner and Shorey succeeded in isolating from various soils the diamino acids arginine⁴ and histidine, as well as the pyrimidine⁵ derivative, cytosine, and the purine⁶ bases, xanthine and hypoxanthine. Prior to that Shorey extracted from Hawaiian soils a compound which he identified as picolinicarboxylic acid.⁷ Among the decomposition products of Michigan peat the monoamino acids leucine⁸ and isoleucine were isolated and identified by Robinson, who also quantitatively determined the amino⁹ nitrogen in the peat by Van Slyke's¹⁰ nitrous acid method.

Adding, as the above researches do, to our knowledge concerning the nature of organic compounds in soils, yet it seems desirable, if not im-

¹ *Z. physiol. Chem.*, 27, 95 (1899); 29, 47 (1900); 29, 136 (1900); 31, 215 (1900). *THIS JOURNAL*, 25, 323 (1903).

² *Biochem. Z.*, 7, 47 (1907); 7, 407 (1908).

³ *THIS JOURNAL*, 32, 396 (1910); 33, 1226 (1911). *Technical Bull.* 4, (1909) Mich. Agr. Exp. Sta.; *Research Bull.* 1, (1911) Iowa Agr. Exp. Sta.

⁴ *J. Biol. Chem.*, 8, 381 (1910).

⁵ *Ibid.*, 8, 385 (1910). *Bull.* 74, Bureau of Soils, U. S. Dept. Agr.

⁶ *Ibid.*

⁷ *Ann. Rept. of Hawaii Agr. Exp. Sta.*, 1906, p. 55.

⁸ *THIS JOURNAL*, 33, 564 (1911).

⁹ *Michigan Agr. Expt. Sta., Techn. Bull.* 7, p. 11.

¹⁰ *Ber.*, 43, 3170 (1910).

perative, to throw more light upon a question of such significance, bearing in mind that the question is of fundamental importance to agriculture since it is intimately connected with the momentous biological processes of ammonification, nitrification and denitrification. It is for this reason that it was decided to investigate an additional number of plots as to the nature of the organic nitrogen contained in them. The plots S, T, V, herein examined, form a part of the experiment station field which is situated on the Wisconsin drift. The plots, having the size of one-tenth of an acre each, were treated as follows: In 1906 they received a heavy application of manure, in 1907, 1908 and 1909 none. They grew corn in 1905 and 1906, oats and clover in 1907, corn in 1908 and 1909. The soil samples were taken in the fall of 1909 and represent composite samples of twenty-four borings taken from each plot to the depth of seven inches.

It was soon ascertained that the proportion of ammoniacal and nitric nitrogen in the plots under consideration was insignificant, from which it followed that the soil nitrogen consisted of organic nitrogenous compounds. Their separation into acid amides, diamino acids and monoamino acids was performed according to the Hausmann-Osborne method, namely by distilling the evaporated acid extract of the soil with mag-

TABLE I.—PERCENTAGE OF NITROGEN IN THE VARIOUS COMPOUNDS.

Plot.	Gram.	% of oven-dried soil.	% of total soil nitrogen.	% of nitrogen in solution.
S. Total nitrogen in solution (obtained by boiling with hydrochloric acid).....	0.16069	0.1844	87.37	100.00
Ammoniacal nitrogen.....	0.00081	0.0009	0.44	0.50
Nitrogen of acid amides.....	0.05397	0.0619	29.35	33.59
Nitrogen of diamino acids.....	0.02773	0.0318	15.08	17.26
Nitrogen of monoamino acids (difference from 100).....	0.07818	0.0897	42.51	48.65
T. Total nitrogen in solution (obtained by boiling with hydrochloric acid).....	0.20247	0.2199	92.41	100.00
Ammoniacal nitrogen.....	0.00099	0.0011	0.45	0.49
Nitrogen of acid amides.....	0.06789	0.0737	30.99	33.53
Nitrogen of diamino acids.....	0.04029	0.0438	18.39	19.90
Nitrogen of monoamino acids (difference from 100).....	0.09330	0.1013	42.58	46.08
V. Total nitrogen in solution (obtained by boiling with hydrochloric acid).....	0.12675	0.2216	88.98	100.00
Ammoniacal nitrogen.....	0.00062	0.0011	0.43	0.49
Nitrogen of acid amides.....	0.04207	0.0735	29.53	33.19
Nitrogen of diamino acids.....	0.01797	0.0314	12.61	14.18
Nitrogen of monoamino acids (difference from 100).....	0.06609	0.1155	46.40	52.14

nesia, which gave, in the form of ammonia, all the nitrogen corresponding to the amides present in the soil. The residue which remained on distillation of the soil extract with magnesia was thoroughly extracted with water and concentrated to 100 cc., to which sulfuric acid and enough phosphotungstic acid were added to throw down the diamino acids present in the extract. The determination of the nitrogen in the washed phosphotungstic acid precipitate gave the amount of the diamino nitrogen. The percentage of the monoamino nitrogen was obtained by subtracting the sum of ammoniacal, amido, and diamino nitrogen from 100. The results secured are recorded in Table I.

While the phosphotungstic acid precipitate and the filtrate from that precipitate, in the case of protein decomposition products, virtually represent diamino acids and monoamino acids respectively, it may not hold good for soil extracts. However, the facts presented in Table II go to show that the substances designated in Table I as diamino and monoamino acids actually display reactions and possess properties which are characteristic of those compounds.

As was pointed out elsewhere,¹ not all of the nitrogen obtained by the Hausmann-Osborne method as such, of diamino and monoamino acids actually represent, diamino and monoamino nitrogen, but that a portion of that nitrogen belongs to classes other than amino acids. To ascertain just what proportion of that nitrogen is virtually made up of diamino and monoamino acids, the soil extracts from the plots S, T, V were subjected to formaldehyde titration. Before presenting the results, however, a few notes may not be amiss in connection with the formaldehyde titration method. In order to avoid mistakes, it is necessary to use for titration not too small amounts of the amino acids; the greater the quantity employed for the formaldehyde titration the more reliable are the results. Further, it is of advantage to start the formaldehyde titration, not in the alkaline but in the acid state, *i. e.*, the soil extract to be titrated is slightly acidified with hydrochloric acid so as to require, say, from one to three cc. of 0.2 *N* barium hydroxide. The operations in question are conveniently carried out as follows: The soil extract containing amino acids, upon examination of the optical activity, is made up to a definite volume, say, to 60 cc., for which the nitrogen in 15 cc. is determined by the Kjeldahl method to ascertain the total nitrogen present in the sample, 15 cc. are titrated in the ordinary way to determine the acidity of the substance, and two portions of 15 cc. each are titrated with formaldehyde to find the increase of acidity due to the reaction with formaldehyde. These three operations furnish all the data which are necessary for the calculation of the percentage of diamino or mono-

¹ THIS JOURNAL, 33, 1239 (1911).

TABLE II.

Diamino acids.		Monoamino acids.	
Reactions.	Rotation.	Reaction with formaldehyde.	Rotation.
The diamino acids extracted from the various plots (S, T, V) displayed the following reactions:		The monoamino acids extracted from the soils examined, on being mixed with neutralized formaldehyde, immediately turned acid, thus indicating the presence of carboxyl and amino groups.	
1. Phosphotungstic acid gave a heavy, white precipitate.	S. The diamino acid solution containing 0.006 g. nitrogen, on acidulating with hydrochloric acid, rotated in the 2 dm. tube $+0.09^{\circ}$ (Ventzke).		S. The monoamino acid solution, with 0.042 g. nitrogen, having been acidulated with hydrochloric acid, showed in the 2 dm. tube the rotation $+0.61^{\circ}$ (Ventzke).
2. Phosphomolybdic acid gave a yellow precipitate.	T. The rotation of the acidulated diamino acid solution, with 0.008 g. nitrogen, was $+0.22^{\circ}$ (Ventzke).		T. The monoamino acid solution containing 0.040 g. nitrogen, rotated -0.75° . When acidulated with 5 cc. concentrated hydrochloric acid, the same solution showed the rotation $+0.1^{\circ}$ (Ventzke).
3. Mercuric chloride gave a grayish white flocculent precipitate.	V. The diamino acid solution, with 0.007 g. nitrogen, having been strongly acidulated with hydrochloric acid, showed the rotation of $+0.20^{\circ}$ (Ventzke).		V. The aqueous solution of the monoamino acids, extracted from about 150 grams soil, showed the rotation -0.73 (Ventzke). Acidulated with 3 cc. concentrated hydrochloric acid, the same solution showed the rotation $+0.5^{\circ}$ (Ventzke).
4. Silver nitrate gave a grayish or yellowish white precipitate, soluble in excess of ammonia.			
5. Picric acid either failed to give a precipitate, or the precipitate obtained after some time was quite insignificant.			
6. The aqueous solution of the diamino acids was strongly alkaline.			
7. Addition of neutralized formaldehyde to the alkaline solution caused it to turn acid, pointing to the presence of carboxyl and amino groups.			

amino acids present in the substance under examination. The results are given in Table III.

While the data before us to a certain degree modify the results reported in previous publications, especially as far as the percentage of diamino and monoamino acids is concerned, yet this modification does not go far enough to shift the ratio of the acid amides to the diamino and monoamino acids. Here, as in the earlier publications, the percentage of monoamino acids is predominant, next in proportion follow the acid amides, and finally the diamino acids. The percentage of the ammoniacal nitro-

TABLE III.

Diamino acids.

Plot S.—The soil extract containing diamino acids was made up to 60 cc., of which 15 cc. were titrated in the usual way and required 0.2 cc. 0.2 *N* barium hydroxide, and 2 portions of 15 cc. each were titrated with formaldehyde and required on the average 0.6 cc. 0.2 *N* barium hydroxide. This means that the increase of the acidity caused by the presence of diamino acids corresponds to 0.4 cc. 0.2 *N* barium hydroxide. Unfortunately, 15 cc. of the soil extract oxidized according to Kjeldahl were lost, so that the percentage of the diamino acids could not be calculated.

Plot T.—The soil extract supposed to contain diamino acids was made up to 60 cc. The nitrogen determination in 15 cc. showed that they contained 0.006 g. nitrogen. 15 cc. titrated in the ordinary way required 1.47 cc. 0.2 *N* barium hydroxide; two portions of 15 cc. each titrated with formaldehyde required 2.04 cc. 0.2 *N* barium hydroxide. This means that the 60 cc. substance, through formaldehyde, increased in acidity equivalent to 2.28 cc. 0.2 *N* barium hydroxide or 0.01280 g. nitrogen (53.3 per cent.), if lysine alone were present; or 0.01921 g. nitrogen (80.0 per cent.), if histidine alone were present; or 0.02561 g. nitrogen (106.7 per cent.), if arginine only were present. While these figures do not give the actual percentage of each one of the diamino acids, they do show that a large portion of what is given in Table I as nitrogen of diamino acids actually represents diamino nitrogen.

Plot V.—60 cc. of the soil extract were analyzed as in S. It was found that the increase of acidity through formaldehyde was equal to 0.67 cc. 0.2 *N* barium hydroxide. The Kjeldahl determination in 15 cc. of this solution was unfortunately lost by accident, which rendered the calculation of the percentage of diamino nitrogen impossible.

Monoamino acids.

Plot S.—Sixty cc. of the soil extract containing monoamino acids were treated as follows: the nitrogen determination in 15 cc. gave 0.01407 g. nitrogen; 15 cc. were titrated and required 2.2 cc. 0.2 *N* barium hydroxide; two portions of 15 cc. each were titrated after adding formaldehyde and required on the average 5.61 cc. 0.2 *N* barium hydroxide. This means that 3.41 cc. 0.2 *N* barium hydroxide equivalent to 0.00957 g. nitrogen, or 68.02 per cent. of what is given in Table I as nitrogen of monoamino acids, actually represent monoamino nitrogen. The other 31.98 per cent. belongs to classes other than monoamino acids.

Plot T.—The titration with formaldehyde of 60 cc. substance, with 0.0552 g. nitrogen, showed that 82.03 per cent. of what is given in Table I as nitrogen of monoamino acids actually represent monoamino nitrogen, the rest consisting of nitrogenous compounds other than monoamino acids.

Plot V.—The substance containing monoamino acids was analyzed with the following result: 15 cc. were found to contain 0.0097 g. nitrogen. The increase of acidity in 15 cc. substance, due to the reaction with formaldehyde, was equivalent to 2.97 cc. 0.2 *N* barium hydroxide, which is equal to 0.00834 g. nitrogen. Or 85.98 per cent. of what is recorded in Table I as nitrogen of monoamino acids actually represent monoamino nitrogen.

gen is insignificant. In comparing the results, the differences of which may in part be due to some difference between the soils S, T, V, on the

one hand, and Θ ,¹ U, on the other, it is to be borne in mind that whereas in laboratory or pot experiments one can easily get good average samples, it is quite different with field or plot experiments. In the first place it is not an easy task to obtain one or several tons of manure, hay or straw as a uniform and homogeneous mass. Nor is it possible absolutely evenly to distribute such organic materials throughout the plots. Likewise, it is very difficult, if at all possible, to get a truly average soil sample from a plot of the size of one-tenth of an acre. It is for these reasons that samples from the same plot, and still more so from different plots, though treated with the same organic materials, may in some measure differ from each other. This may account for some differences in the results reported, yet, on the whole, the data secured in the above experiments confirm the data presented in the former¹ publications.

Conclusions.

1. The principal portion of the acid-soluble organic nitrogen, contained in the soils investigated, is made up of acid amides, monoamino acids and diamino acids.

2. The larger part of the phosphotungstic acid precipitate, recorded in Table I as nitrogen of diamino acids, actually represents diamino nitrogen, the smaller part belonging to classes other than diamino acids.

3. In the case of the filtrate from the phosphotungstic acid precipitate, presented in Table I as nitrogen of monoamino acids, it was found that from 68.02 to 85.98 per cent. of that filtrate represent in fact monoamino nitrogen, the rest (from 31.98 to 14.02 per cent.) consisting of nitrogenous compounds other than monoamino acids.

[FROM THE LABORATORY OF FERTILITY INVESTIGATIONS.]

THE ISOLATION OF CREATININE FROM SOILS.²

BY EDMUND C. SHOREY.

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In the course of investigations into the nature of the organic constituents of soils a crystallin organic compound was isolated and identified as creatinine.

Reactions indicating the presence of this compound were first observed in a solution of a portion of the soil organic matter obtained in the following manner: The soil was treated with 2% sodium hydroxide solution for half an hour, and then without separation of the alkaline extract from the soil, acetic acid in slight excess was added and the acid solution filtered from the soil and precipitate formed. The acid filtrate was neutralized with sodium hydroxide and, without filtering, a solution of

¹ *Loc. cit.*

² Published by permission of the Secretary of Agriculture.

lead acetate added and the precipitate formed, separated by filtration. On the addition of ammonia to the filtrate a further precipitate was produced, which was filtered off, washed, and decomposed by hydrogen sulfide. The filtrate from lead sulfide was concentrated to a small volume and was found to give the Jaffé, Weyl, and Salkowski color reactions for creatinine.

It was further found that if the filtrate from the neutral lead acetate precipitate was made alkaline with sodium hydroxide instead of ammonia, and the resulting precipitate decomposed and concentrated, the color reactions were obtained more strongly, indicating a more complete precipitation of the creatinine by this means.

From the known behavior of creatinine when treated with lead acetate in alkaline solution it was evident that neither of the methods of precipitation mentioned would result in complete separation of the creatinine present, and for the isolation of this compound recourse was had to another method.

The method by which creatinine was first isolated from soils, and already noted elsewhere,¹ was to apply to an alkaline soil extract a method recommended by Balke² for the separation of purine bases, and used for that purpose in this laboratory.³ This method depends on the fact that when there is precipitation of cuprous oxide from Fehling's solution by a reducing compound, purine bases and some related compounds combine with the cuprous oxide and are found in the precipitate. Creatinine behaves in this way, as was first pointed out by Masche.⁴

The method as applied to the isolation of creatinine from soils was carried out as follows: An alkaline extract of the soil, made by treatment for a short time with 2% sodium hydroxide, was made exactly neutral with acetic or sulfuric acid and filtered. The neutral filtrate was heated to boiling and a little glucose added and then Fehling's solution, slightly in excess of that required by the glucose present. The precipitate formed was separated by filtration, well washed, and decomposed by hydrogen sulfide. The filtrate from the copper sulfide was concentrated to a small volume under reduced pressure, a small quantity of a concentrated solution of zinc chloride and a little sodium acetate added, and the whole allowed to stand several days. Within a few hours crystals began to form, and in 48 hours these were observed to have the characteristic appearance of creatinine zinc chloride. The crystals were separated from the mother liquor by filtration, or, when the quantity of material was very small, by placing the whole mass on a porous plate. After separation the crystals

¹ *Science*, 33, 340 (1911).

² *J. prakt. Chem.*, [2] 47, 537 (1893).

³ *Bull.* 74, Bureau of Soils, p. 41 (1910); *J. Biol. Chem.*, 8, 391 (1910).

⁴ *Z. anal. Chem.*, 1878, 134.

were washed with a little cold water, suspended in water and boiled with some freshly precipitated lead hydroxide, filtered, and the filtrate concentrated to a small volume; on standing a short time crystals formed having the appearance, solubility, and color reactions of creatinine.

From another portion of the same soil from which creatinine had been obtained by the method just outlined, creatinine was also obtained by alcoholic extraction. About 100 grams of air-dried soil were extracted in a Soxhlet extractor for 7 hours with 95% alcohol. The alcohol was removed from the colored extract so obtained by evaporation, water being added to keep the volume constant. The aqueous solution was filtered from resinous and fatty matter and evaporated to a small volume under reduced pressure. The concentrated solution gave all the color reactions for creatinine strongly, and on treatment with zinc chloride gave, after standing two days, crystals of the characteristic creatinine zinc chloride.

Creatinine was also obtained from the same soil by simple extraction with water. About 5 kilograms of soil were extracted with cold distilled water in a percolator until 8 liters of extract had been obtained. This was concentrated to about 100 cc. by evaporation under reduced pressure, and filtered from a small quantity of insoluble matter present. The solution so obtained gave all the color reactions for creatinine strongly, and on treatment with zinc chloride, crystals of the characteristic creatinine zinc chloride were formed. From these, by treatment with lead hydroxide in the manner already described, crystalline creatinine was obtained.

Creatinine in water solution gives a number of color reactions that have been depended on largely as indicating or proving the presence of this compound in fluids such as urine.

Jaffé's Reaction.—If a solution of creatinine be made alkaline with sodium hydroxide and then a few drops of picric acid solution added, a red color is formed.¹ The color, which is similar to that of a concentrated solution of potassium dichromate, becomes orange on dilution. A quantitative colorimetric method for determining creatinine based on this reaction has been devised by Folin² and has been almost universally adapted in determining the quantity of this compound in urine. In the use of this reaction for either qualitative or quantitative purposes the absence of other compounds that give a similar color or that give a color that would obscure the one given by creatinine must of course be assured. In urine the only compound of this nature likely to be present is acetone, the presence of which can, of course, be easily determined. In solutions or extracts, however, containing soil organic matter there is the possi-

¹ *Z. physiol. Chem.*, 10, 399 (1896).

² *Ibid.*, 41, 223 (1904).

bility of other compounds that may simulate or obscure the color given by creatinine, but whose presence can not be definitely determined, because of lack of sufficient methods. Levulinic acid and furfural both give the Jaffé reaction strongly, and while neither have been definitely identified as present in soils, there are some indications of the presence of the former, and the latter might very easily be present or formed in soil extracts at some stage in the operation.

Weyl's Test.—A watery solution of creatinine to which a small quantity of a solution of sodium nitroprusside has been added gives on the addition of sodium hydroxide a red color which soon changes to yellow.¹ As with the Jaffé reaction, the presence of certain other compounds may interfere with the use of this test either by giving a color that obscures the one given by the test, or giving a similar one. Levulinic acid gives under the conditions of this test a color similar to that given by creatinine, and this test with others has been used to establish the presence of levulinic acid in the decomposition products of nucleic acid.² Furfural and the products resulting from heating pentose-yielding material with acid give a similar color, although in no case is the fading of the red color to yellow as pronounced as with creatinine. The dark purple color given by sulfides in the presence of sodium nitroprusside and sodium hydroxide would, of course, obscure the color given by creatinine, and, as was noted in the case of Jaffé's reaction, there are probably in soil extracts unknown compounds that give either a similar color or one that would obscure the one given by creatinine.

Salkowski's Reaction.—If the yellow solution resulting from Weyl's test be acidified with acetic acid and then heated, the solution turns green, then blue, and Prussian blue is precipitated, if much creatinine is present.³ Both levulinic acid and furfural give the final blue color and precipitate, but in the case of levulinic acid the solution after the addition of acetic acid and before heating is purple. The reagents alone will give the final blue color and precipitate if the solution before acidifying be allowed to become warm.

Since soil extracts or solutions prepared from them may contain compounds that are known to give color reactions similar to those given by creatinine, and since there is the possibility of the presence of others as yet unknown, it is evident that results obtained with the color tests usually considered indicative of the presence of creatinine can not be considered conclusive proof of the presence of this compound in the soils from which the soil extracts were prepared.

When indications of the presence of creatinine are obtained by any

¹ *Ber.*, 11, 2175 (1878). Arnold, *Z. physiol. Chem.*, 49, 397 (1906).

² Inouye, *Z. physiol. Chem.*, 42, 116 (1904).

³ *Z. physiol. Chem.* 4, 133 (1880); 9, 127 (1885).

of the color tests just described, this can best be confirmed and established by the preparation of the creatinine zinc chloride $(C_4H_7ON_3)_2ZnCl_2$. This salt, almost insoluble in alcohol and difficultly soluble in water, is formed when concentrated solutions of creatinine and zinc chloride are brought together in the absence of free mineral acids, a condition usually obtained by the addition of a little sodium acetate. When any large quantity of creatinine is treated in this way there is immediate precipitation, but when small quantities are being dealt with precipitation does not begin for several hours and is not complete for several days. The crystals of this salt are quite characteristic in form, although this form is so modified by the concentration of the solution, the presence of other substances, and other conditions that they appear to differ widely. A study of the form assumed when the crystals first appear, and of their growth, and of the form assumed on recrystallizing, soon results in familiarity with the characteristic appearance, so that the compound can be readily identified, no matter what form it may assume. Usually it appears in balls with radiating structure, due to their being made up of fine needles. Under other conditions its first appearance may be in star-like plates which eventually assume the form of bunches of radiating needles or plates. If the crystallization is slow, the plates may grow to a well-developed form. Under still other conditions the radiating needles are bunched in tufts rather than balls. This last form is the one assumed by the pure compound when a concentrated solution is cooled rapidly.

When sufficient creatinine zinc chloride can be prepared pure, its identification by the method of preparation, solubility, and crystallin form may be supplemented by analysis, although once familiarity with the characteristic behavior and appearance of this compound is acquired, this is not essential. A preparation of creatinine zinc chloride made from an alkaline soil extract in the manner already described was purified by recrystallization, dried on a porous plate, and then in a desiccator, and nitrogen and zinc oxide determined in the following manner: A portion of the creatinine zinc chloride, 0.3600 gram, was digested with a small quantity of sulfuric acid and a little potassium sulfate, as in the Gunning modification of the Kjeldahl method for total nitrogen. The resulting solution was made alkaline with sodium hydroxide and distilled into standard acid in the usual manner. After the removal of the ammonia by distillation the solution was made acid with acetic acid and the zinc in solution precipitated by hydrogen sulfide, the zinc sulfide collected, the precipitate and filter paper treated with nitric acid, dried, and carefully ignited and weighed as zinc oxide. The analysis gave the following figures:

Calculated for $(C_4H_7ON_3)_2ZnCl_2$: N, 23.16; ZnO, 22.45

Found:

N, 23.22; ZnO, 22.31

The formation of free creatinine from creatinine zinc chloride by boiling with lead hydroxide in the manner already described, the crystallization of the creatinine so obtained, and observations regarding its crystallin appearance, solubility, and color reactions may be resorted to in further confirmation of the identity of the compound. The crystallin appearance of creatinine, monoclinic plates or prisms, is, however, not characteristic enough to form the basis of identification.

At this point the question naturally arises whether the isolation of creatinine by the methods described indicates or proves the presence of creatinine in the soil. In deciding this question in the case of other organic compounds isolated from soil the conclusion that the compounds in question must be in the soil as such was based on the fact that all the knowledge of the behavior of the compounds and their antecedents indicated that they could not be formed by any of the treatments to which the soil or soil extracts had been subjected. In the case of creatinine the question is complicated: first, by the fact that nothing is definitely known regarding its antecedents, *i. e.*, what complex molecule, if any, it is derived from; and, second, by the fact already mentioned that creatinine is readily changed to creatine and *vice versa* according to the conditions imposed. Consequently, from general considerations only, it might seem that the creatinine isolated by methods which involve chemical reagents and heat might be derived from creatine or some unknown more complex compound from which creatinine was easily split off. More detailed consideration, however, of the methods involved effectually disposes of the possibility that the creatinine is wholly derived from creatine. While the transformation of creatine and creatinine back and forth into each other is comparatively easy, Folin has shown¹ that it is not so easy as many investigators have assumed. All the operations in the methods used, except the final concentration, were such as would result in the change of creatinine back to creatine rather than otherwise. The alkaline extraction and boiling with Fehling's solution would no doubt bring about this change to some extent so that the creatinine finally obtained was that which had resisted this treatment. The final concentration of the aqueous solution at a low temperature might form some creatinine from creatine, but investigation has shown that this change could be but slight and could never involve the whole of the creatine if it were present. Treatment of these solutions by boiling for several hours with acid resulted in but slightly increased colorimetric readings for creatinine. In other words, the small quantity of creatine present shown by this method was out of all proportion to what would

¹ "The Chemistry and Biochemistry of Creatine and Creatinine," Festkrift, Olof Hammersten, III.

remain after evaporation under reduced pressure, if creatine only had been present in the original solution.

The question of the possibility of the creatinine obtained being formed during the treatment from some more complex antecedent easily broken down, unfortunately can not be disposed of until some definite information regarding such a complex, if there is one, is available.

In the light of all the knowledge available and on consideration of the bearing of the methods on the final product it seems safe to conclude that a considerable portion at least and probably all of the creatinine isolated from soils is present in the soils as such.

The possible relation of creatinine to more complex compounds found in the soil or added to soil in dead vegetation is still obscure, but a few observations made in this connection are worthy of record. Nucleic acids of unknown constitution have been found in several soils.¹ Both nucleic acid from soil and yeast nucleic acid prepared by Merck have been found to give the color reactions for creatinine after heating or even warming for a few minutes with dilute hydrochloric acid. From a solution of yeast nucleic acid treated in this way crystalline creatinine zinc chloride was prepared. It was found, however, that on washing the nucleic acid with cold dilute hydrochloric acid the nucleic acid no longer had the property of giving creatinine on heating with acid. The hydrochloric acid washings, however, after heating showed the creatinine reactions. Whether the explanation of this lies in the inclusion of some creatine in the nucleic acid or whether creatinine is actually split off from the nucleic acid or some complex included with it is as yet unknown. Phytin, or hydroxymethylene diphosphoric acid anhydride, is an organic compound that occurs in the seeds of many plants and must find its way into the soil. So far, this compound has not been isolated from any soil, but it was found that a crude preparation prepared from wheat bran gave on heating with hydrochloric acid a solution which gave the color reactions of creatinine, and from this solution crystals of creatinine zinc chloride were prepared. On purifying the phytin, however, in the usual way by precipitating it several times as the barium salt² it likewise no longer had this property.

The relation of the creatinine to plants and plant products generally has been already treated in papers from this laboratory³ and the only further observations that will be made here bearing on the relation of creatinine to soil organic matter have to do with that added in agricultural practice, *viz.*, organic manures. Creatinine has been found both in stable manure and in fresh cowpea vines as used in green manuring.

¹The results of the investigation on nucleic acids in soils will be reported later.

²Patten and Hart, *Am. Chem. J.*, 31, 564 (1904).

³Sullivan, *THIS JOURNAL*, 33, 2035 (1911) and Skinner, *Bot. Gaz.* (1911).

A sample of well-rotted stable manure was extracted with water and the solution allowed to stand until further fermentation had ceased. From this extract creatinine was isolated by precipitation with Fehling's solution in the same manner as from soil extracts. The resulting solution gave the color reactions for creatinine and crystals of both creatinine zinc chloride and creatinine were prepared from the material isolated. Green cowpea vines were crushed and extracted with cold alcohol, the alcohol evaporated at a low temperature, and water added to keep the volume constant and the solution filtered from insoluble matter. From this solution creatinine zinc chloride was prepared by precipitating the creatinine with Fehling's solution and subsequent treatment with zinc chloride and also by treating the concentrated aqueous solution directly with zinc chloride.

The work so far done on the quantitative determination of creatinine in soils is but preliminary and no definite statement regarding the quantity present in soils can be made other than that it is small and apparently but a small portion of the total organic matter. The following facts bearing on this question were established. It is much more easily extracted from soil by alcohol than by water. Usually enough could be obtained by extracting 100 grams of soil with alcohol to establish its identity, but to accomplish this by aqueous extraction several pounds of soil were usually necessary. In spite of this fact, alcohol extraction does not offer an available method for quantitative determination, as is shown by the following experiment: One hundred grams of soil were extracted with alcohol until the concentrated extract no longer gave any reaction for creatinine. Ten milligrams of creatinine were then added and the soil extracted with alcohol again, and the creatinine determined colorimetrically in the extract obtained. After 14 hours of continuous extraction only three-tenths of a milligram of creatinine was found in solution, and a second extraction of 7 hours gave an amount too small to be determined. The color obtained was not greater after heating these extracts with acid, showing that the creatinine had not been extracted and changed to creatine. Since both water and alcohol extraction seemed unavailable as the basis of a method, attention was given to alkaline extraction. In attempting to carry this out quantitatively several difficulties are met. The complete extraction of the organic matter from soil with dilute alkali is slow and results in a very large volume of solution. Again this solution is darkly colored and the use of a colorimetric method is out of the question unless there is removal of the color and concentration of the solution. It is possible that alkaline extraction and precipitation of the creatinine from the solution with Fehling's solution or in some other way will ultimately afford a means of determining this compound in soils, but so far these attempts have not given satisfactory figures.

The quantity of creatinine that has been found in soils by any of the methods tried, while small, and representing but a small portion of the organic matter, is by no means negligible, being usually several parts per million of soil and usually equal to and sometimes in excess of the quantity of nitrates normally present.

There is every indication that in no case was there complete extraction of the creatinine, and it is moreover possible that this organic soil constituent is a fluctuating quantity, being generated by bacterial or other biological agencies in the soil under certain conditions, and being changed or removed from the soil by growing plants under other conditions.

The initial work on the isolation of creatinine from soil was done with a sample of Volusia silt loam from New York. The sample was from a field that had been in cultivation for many years. At the time the sample was taken and for several years previous the crops on the field had been very poor. So far as could be ascertained the field had never had any application of either commercial fertilizer or stable manure.

After the identity of the compound isolated from the Volusia silt loam was established as creatinine a number of other samples of soil were examined for the presence of this compound. Comparatively few soils have been examined, but so far no soil has been found in which the presence of creatinine was not indicated by the color reactions given by the extract.

Creatinine zinc chloride in addition to color reactions was obtained from samples of the following soils:

Frankstown stony loam from Pennsylvania. This sample was taken from a field that had been in cultivation 30 years, but had recently lain idle for 3 years. When put in cultivation again the crops were still very poor.

Clarksville silt loam from Kentucky. This sample was from an area where the crop yields were fair and the soil responded well to applications of stable manure.

Dunkirk clay from New York. Fair crop yields had been obtained on the field where the sample was taken.

It would seem, then, that creatinine is probably a normal and constantly occurring constituent of soils. While the soils examined have all been under cultivation some years there is no theoretical reason for concluding that virgin soils differ from cultivated ones in this respect except perhaps in quantity.

NEW BOOKS.

Modern Science Reader with special reference to Chemistry. Edited by ROBERT MONTGOMERY BIRD, Ph.D., Collegiate Professor of Chemistry in the University of Virginia, 323 + viii pages. New York: The Macmillan Company. 1911.

"This book provides a partial course of reading in Chemistry for college men and general readers, and indicates further matter of an interesting and instructive nature. * * * It is our experience with college men that parallel reading, more than any other influence, conduces to interest in textbook matter, *especially in first-year courses in science*. It broadens the student's views, enlivens the subject and shows its bearing upon the work and problems of life. * * * We have had in mind, also, persons who are seeking knowledge without the aid of a teacher. Definit information for reading and home study is given. * * * We have endeavored, particularly, to choose articles which are suggestive * * * and will broaden the reader's outlook on science."

These extracts from the preface will indicate the scope of the book. It contains 28 articles, beginning with Sir William Crookes' "Romance of the Diamond," from a recent *North American Review*, and ending with Remsen's "Unsolved Problems of Chemistry," from *McClure's*. Among other topics are explosives, artificial silk, steel rails and alloy steels, coal, coal-tar, the yeast cell, radioactivity, and electrons. Sir Andrew Noble, John A. Mathews, Vivian B. Lewes, J. W. Richards, Kopp, Madame Curie, and Sir Oliver Lodge are among the authors quoted.

Many teachers will find in this book interesting collateral readings for their students and it is heartily to be recommended.

JAS. LEWIS HOWE.

Handbuch der Mineral-Chemie. EDITED BY C. DOELTER AND OTHERS. Bogen, 11-20. Price, M. 6.50. CONTENTS.—The carbonates of sodium concluded. The carbonates of sodium and the alkaline earths by Wegscheider. Potassium and ammonium carbonate by Wegscheider. Magnesium carbonate by Leitmeier. Genesis and occurrence of magnesite by Redlich. Uses of magnesite by Redlich. The hydrates of magnesium carbonate by Leitmeier and d'Achiardi. Calcium carbonate by Leitmeier and analytical methods by Dittrich.

The peculiar arrangement of this book according to which all the matter bearing on one topic is not given in the same place is inconvenient, to say the least, and will hardly meet with approval from most readers. It was owing to this unfortunate classification that the writer made an unwarranted criticism of the first instalment of this work, which he is here glad to correct. The constants of calcium carbonate, the omission of which was criticized, are given in detail in the second instalment. The information in Bogen 11-20 seems to be very complete and very recent work is included.

E. T. ALLEN.

Alexander Smith

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AN EARLY PHYSICAL CHEMIST—M. W. LOMONOSSOFF.¹

BY ALEXANDER SMITH.

Received December 28, 1911.

At the present day, it seldom happens that due credit is not given to each chemist for any new facts which he may add to the sum of chemical knowledge and, conversely, it is usually an easy matter to attach to any given fact the name of the investigator who first discovered it. For reasons which, in part, at least, are obvious, these conditions are not always so easy to fulfil in the case of the fathers of the science. It is certain, at all events, that frequently recognition has here been long delayed and, even where the most fundamental facts are concerned, the determination of the parentage has had repeatedly to be revised.

At the very start, there is the difficulty in settling what constitutes discovery. Scheele's preparation of oxygen undoubtedly took place a year or two before Priestley's, but his publication of the results was delayed until three years after Priestley's, and priority in discovery is generally held to require priority in publication.

Again, Paracelsus obtained what is now known as hydrogen by the action of iron filings upon vinegar, but Cavendish defined the substance by its properties, and so the discovery dates from 1766. Liebig prepared bromine, but set the sample aside, believing it to be a chloride of iodine, and Balard, who prepared the substance later and recognized it to be a new halogen, became the discoverer. Similarly, a hundred years before Priestley's time, Borch (1678) prepared what is now known as oxygen in large quantities by heating saltpeter, but he failed to ascertain any of its properties; and again, forty-five years before Priestley's experiment, Hales collected the gas from the same source over water (the first record

¹ Presidential Address delivered before the American Chemical Society at Washington, December 28, 1911.

of any attempt to collect a gas in this way) and obtained, by measurement, 97% of the theoretical amount. But Priestley, on Aug. 1, 1774, liberated it from mercuric oxide. A lighted candle happened to be standing before him at the moment. By pure chance, as he himself says, and without any particular reason which he could afterwards recall, he immersed the candle in the gas and found that the combustion was unusually brilliant. He thus ascertained one distinct property of the substance and became the discoverer of oxygen. True, he thought at first that it was a compound of nitrous acid, earth and phlogiston, and only in the light of the views of Lavoisier and others, and after long delay, did he accept in 1786 the conclusion that it was an elementary substance. It may be noted that, although Scheele was a better experimenter, his idea of the nature of oxygen was not much clearer. He thought that fire-air (oxygen) united with phlogiston to give heat, and that the last was a compound of the first two. Evidently, in those days, isolating the substance, and defining one or two of its properties, together conferred discoverer's rights, no matter how grotesquely the nature of the substance was misunderstood.

I say, "in those days," for Curie made several compounds of radium, establishing their relations to one another, and is justly held to be the "discoverer of radium," although no isolation of the element was attempted. Now that the science has developed, isolation can be dispensed with, and, in point of fact, was omitted in most of the exploratory work among the rare metals. If this principle could have been applicable in earlier days, several of the decisions of chemical history might have been reversed. A hundred years before Priestley's time, Mayow (1669) had shown by conclusive experiments that atmospheric air was made up of two components, of which the active one formed 25% of the whole. In measuring the amount, he employed the same reaction subsequently used by Priestley, namely, removal of the oxygen by the introduction of nitric oxide and absorption of the product in water. But, whereas Priestley was thereby estimating the "goodness" of the air, and had no idea that he was dealing with a mixture, Mayow was perfectly clear as to the interpretation of the results. The latter demonstrated that the same component was removed in combustion, by rusting metals, by the alcohol in vinegar-making, and by the blood in respiration. He traced the animal heat of the body to a process analogous to that which heated the mass when marcasite rusted in the air. He identified this active component of the air as a constituent of saltpeter, and particularly of the acid part of this substance, and (like Lavoisier more than a century later) held that it was contained in all acids. Finally, he considered it to be an element, in the modern sense of the word. Unfortunately circumstances conspired to relegate to obscurity all his wonderful work and

magnificently clear reasoning. Mayow was a young physician, and the divergent view-point of Boyle, as an older man and an eminent philosopher, received more attention. Again, the logical conclusiveness of Mayow's proof of the existence of oxygen as a distinct substance was entirely over the heads of his contemporaries, and his way of thinking quite out of harmony with theirs. In this point of view, he came a century and a half too soon. Such a proof, if offered at the present day, would be accepted as conclusive. The final isolation of the element would now be considered a matter of mere routine that could be assigned to a beginner in research, as the basis of his dissertation for the degree of doctor of philosophy. Finally, the clouds of the phlogistic theory soon began to darken the sky of the science, and before long the spread of this remarkable notion, diligently fostered by Stahl who had been born nine years before the appearance of Mayow's work, enveloped chemistry and the whole chemical world in an impenetrable fog. Since the believers in phlogiston started always with one absurd idea as the major premise, namely, that in combustion and oxidation some kind of matter *left* the burning or rusting material, the more rigorous the logic of the subsequent steps in the reasoning, the more certain was the attainment of uniformly false conclusions. The inveterate phlogistian, and everybody down to the time of Lavoisier, not excluding Priestley and Scheele, was forthwith an inveterate phlogistian, saw in simple, almost modern modes of thought like those of Mayow, only the sheerest nonsense. If we all stood habitually upon our heads, naturally any one caught persisting in a tendency to view the universe in the normal way would be instantly adjudged insane. For these various reasons, Mayow's work was first neglected and then forgotten.

The story of Mayow suggests some additional conditions which determine the recognition of a discoverer, and the acceptance of his discovery. How often in the history of science has a dominating but conservative personality diverted attention from younger or less prominent men, or at the least, by hostile criticism, delayed the acceptance of their ideas? The discoverer who occupies a conspicuous social position is, often, more readily detected. Then again, for the dealing of strict justice, the consequences may be almost as unfortunate when the discoverer is a century ahead of his time, like Mayow, as when he is three years late, like Scheele. And finally, an intellectual plague like the phlogistic theory may be epidemic. An infection runs until a milder generation of the infecting organism is gradually evolved, or until the presence of the organism results in physiological changes which automatically give rise to substances that destroy it. Lavoisier was fortunate in arriving upon the scene when the disease was ready to loosen its hold. It was not that his fundamental experiments, upon the subject of air and oxygen, were new—the same

conclusions could have been reached by putting together the work of his predecessors and contemporaries. It was largely because of his personality, and because he arrived at the psychological moment.

I have prefaced my address in this way, in order to furnish a setting for its subject. He lived from 1711 to 1765. He thus was educated, did his life-work, and died in the most virulent period of the phlogistic epidemic. Heat, light and weight were then forms of matter, yet, when he notices them at all, he combats these views, and makes experiments to disprove them. In a day when the jargon of the phlogistian was the only language of polite intercourse among chemists, he speaks and writes the language of modern chemistry—of the most modern chemistry, for he was a physical chemist. Needless to say, he lived at a time far removed from the psychological moment for a man holding such a view-point. Naturally, credit for his discoveries, and they were many, has all been distributed among others. It is quite likely that some of you have never happened to hear his name—the name of Michael Wassiliewitsch Lomonossoff.

Even in Russia, although his work in literary and linguistic lines, his success as a man of affairs, and his investigations as a geographer and a meteorologist had won for him enduring fame, the fact that he was primarily a chemist had been completely forgotten. It was Menschutkin¹ who, a few years ago, rediscovered him as a chemist, reprinted in Russian his scattered memoirs, and collected all that could be found of his manuscripts, letters, and laboratory note-books.

Although trained—chiefly in Germany—by, and along with men who ardently supported the current views, he seems with astonishing ease to have thrown off the prejudices of his contemporaries, and to have achieved a perfectly independent view-point of his own. At that time, the emission of light-matter explained the phenomena of light. Largely through the enormous influence of Newton's selection of the emission theory in preference to the wave theory (first developed by Huygens in 1690), this remained the accepted explanation until after a hard struggle against the influence of Laplace (1817) and others, who were unconvinced, with the explanation of the phenomenon of polarization, by Fresnel, the ether-wave theory finally triumphed. But Lomonossoff discusses (1753-56) the possible motions of ether—progressive, rotatory, and wave-like—identifies the last as the basis of light, and goes in great detail into the nature of ether and the properties of light-waves and the mode of their propagation.

In Lomonossoff's day, heat was also a form of matter. The classical experiment of Rumford was made (1798) thirty years after his death.

¹ M. W. Lomonossoff, as Physical Chemist, St. Petersburg, 1904. See also an article by Menschutkin, *Annalen der Naturphilosophie*, 4, 203.

But so strong was the prejudice that, even then, the proof (by quantitative experiments) that heat could be generated without limit from friction, under conditions such that the addition of any substance or form of matter was impossible, did not carry conviction. Lavoisier believed (with some hesitation it is true) in an imponderable *matière de chaleur*. It was not until after the work of Mayer (1842), who was at first persecuted for his views, and especially after the demonstration by Joule (1855-60) that heat and work were mutually and quantitatively interconvertible, that the theory that heat was matter finally disappeared. Yet Lomonossoff, more than a century earlier (1744-47), in a paper on "The Causes of Heat and Cold," discusses in detail the experimental evidence that motion is a source of heat, and that molecular motions are caused by heating. Radiant heat, of which then little was known, was transmitted by motions of the ether, which he believed to be of the rotatory variety. In all his papers, heat is always a mode of molecular motion. The paper named was the subject of vigorous discussion, particularly in Germany, and after the views contained in it had been sufficiently abused they were consigned to oblivion.

The kinetic molecular theory of gases used to be attributed to Krönig (1856) and Clausius (1857). But Lord Rayleigh discovered in the archives of the Royal Society a very complete form of it, contributed by Waterston in 1845. The state of public opinion among physicists, even then, a century after Lomonossoff's work, may be judged from the fact that the committee of the Society considered the content of the paper to be nonsensical, and refused to permit its public presentation. Lomonossoff's paper, read before the Academy of St. Petersburg in 1744, nearly suffered the same fate, for it was withheld from publication for three years. Starting with the view of Daniel Bernoulli (1738), to the effect that the pressure of gases was due to the impacts of their particles, Lomonossoff proceeded to develop ideas very much like those now held. According to him, for example, a rise in temperature caused increased motion of the particles, and resulted therefore in increased pressure. His theory differs from ours mainly in the fact that rotatory motions played a large part, and that the molecules had rough surfaces. Incidentally he points out that there is no limit to the possible amount of motion, and therefore no maximum of temperature, but that there is a minimum of motion, when the latter becomes zero, and there must therefore be a minimum of temperature. In a later paper (1750) he proves by his hypothesis that the pressure *should* be, as it was then known to be, inversely proportional to the volume. And he goes further, for, with surprising insight, he shows that, with increasing pressure, this relation will no longer hold, since the volumes of the particles themselves are not diminished. The reputed discoverer of this consequence of the theory is Dupré (who was thus anticipated by

115 years), and in 1873 van der Waals finally put the same fact into definit form.

In all this, it must not be supposed that Lomonossoff was simply a reasoner, much less a speculator. The discussion is loaded with a wealth of experimental facts, many of them ascertained by himself. It is especially noteworthy, also, that his experiments, almost without exception, were quantitative. When we remember that the balance is a stubborn instrument, and that its evidence always went contrary to the conclusions of those who pinned their faith to heat-matter and phlogiston, we perceive how completely his habits of work and attitude of mind were out of harmony with those of his contemporaries, and how startlingly independent were his modern ways of experimenting and reasoning.

Before turning to the part of his work that was more especially of a chemical and physico-chemical nature, a few words about his career may be of interest. He was born of peasant parents—Russian peasant parents of the early eighteenth century—about the year 1711, and in a village forty-five miles from Archangel. Opportunities for education there were none. Finally, at the age of 19, he reversed the procedure of the typical boy and ran away to go to school. At 24 he left the school in Moscow to attend the lectures of the professors in the Academy of Sciences in St. Petersburg. At 25 he was sent on a traveling scholarship to Marburg, where he studied chemistry under Wolff. After three years he went to Freiberg, and two years later he returned to St. Petersburg. In both places, when he moved, the Academy had to pay the debts that he had incurred. Upon his return home, he became adjunct professor at a salary of \$900, but the Academy, being poor in money, paid its professors largely by gifts of copies of its publications, a sort of product for which there is an almost infinitesimally small market. A year later we find him in the University, lecturing in Latin on chemistry, geography and the Russian language. Lecturing in Latin upon the Russian language to Russian students! Such simple, blind devotion to a tradition surprises us, even when it occurs in a University. His active experimental work as a chemist began in 1844, when he was 33 years of age, and in 1745 he was appointed to the professorship of chemistry.

After three years of planning, a chemical laboratory was built, and on the 12th of October, 1748, it was opened. The building, a modest one, measured 45 × 36 feet, and was divided into a large room for work and two small rooms for lectures and storage. It cost \$4000, and about \$1800 additional was spent on furnaces and other equipment. Thus, in providing a place for laboratory instruction, as well as for research in chemistry, Lomonossoff was fifty years ahead of Hope in Glasgow and seventy-five years ahead of Liebig.

Lomonossoff's period of greatest chemical activity was compressed

into the nine years that followed the opening of the laboratory, for in 1757 he resigned his chair. During the remaining eight years of his life the numerous activities of a public man, and a diversion of his interests into other scientific lines, interfered with chemical work.

Up to the end of the eighteenth century, there was utter confusion of thought in regard to the composition of materials. In considering the make-up of a specimen, and the changes occurring during an experiment, heat-matter, light-matter and weight-matter, as well as phlogiston, were taken into account. As we have seen, even Scheele interpreted the phenomena he observed upon the theory that heat was an oxide of phlogiston. The composition was often stated in terms of salt, sulphur and mercury, whether there was evidence of their presence or not. The "elements" of Aristotle, and cognate ideas, were used in describing and in thinking about chemical phenomena. In consequence, Priestley thought he had a method of measuring the "goodness" of air—as a quality—when in point of fact he was measuring the amount of oxygen—as a component. With the basal conceptions thus in a state of utter chaos, it is no wonder that the simplest chemical situations were wholly misunderstood, and that the simplest experimental results, being described in terms of non-existent entities, and thought of in terms of non-existent relations, failed of their object. It was Lavoisier who received the credit for setting our ideas permanently in order, by his emphasis upon the significance of the evidence of the balance, and by his setting forth clearly the idea of chemical compounds and their component elementary substances, and by giving a classified list of the latter.

The chemical reformation might have come half a century sooner, however, if Lomonosoff's papers had been more widely known. As we have seen, to him heat and light were not forms of matter and phlogiston had no existence. His forms of matter were the same as ours, and his ideas of chemical composition, what it included and what it excluded, the same as ours. In his "Elements of Mathematical Chemistry" (1741) and in a later paper, "On the Imperceptible Physical Particles, which Compose Natural Materials and in which is to be Found a Sufficient Basis for the Specific Properties" (1742-3), he gives a singularly clear and minute discussion of the whole subject. He distinguishes between the attributes (weight, volume, etc.) of a body or specimen, and the specific properties which characterize a substance. In modern fashion, he defines the "imperceptible particles" or "corpuscles" (molecules), which are portions of a substance, and the "physical monads" or "elements" (atoms) which are not decomposed in chemical change. He draws clearly and in detail the distinction between simple and com-

¹ This and parts of others of his papers are published, in German translation, in Ostwald's *Klassiker*, 178.

pound substances, the latter of which contain the "principia" (elementary forms of matter) in chemical combination. The explanations are in experimental, and not obscure, theoretical terms.

In the paper on "Heat and Cold" (1744-7) he refers to Boyle's experiment, in which lead was sealed up in a retort and heated, when the lead and calx, upon removal, were found to have increased in weight. According to Boyle, this result showed that the heat, which alone could enter through the glass, had weight. Lomonossoff, of course, will not accept this conclusion and points out that the increase in weight of metals when heated in air must be due to union with material from the air, just as their increase in weight when placed in the flame of burning sulfur is due to union with "acid" from the sulfur. Later, in 1756, he repeats Boyle's experiment, and finds that, until the retort is opened and air rushes in, no increase in weight is observable. He thus performed one of Lavoisier's most fundamental and convincing experiments eighteen years in advance, and interpreted it correctly. It is apparent that Lomonossoff's sound views were based upon many quantitative experiments on combustion, although the laboratory note-books containing the details have not yet been found.

But if Lomonossoff anticipated Lavoisier in his work upon the chemical relations of the forms of matter, he went far beyond Lavoisier in his views in regard to the uses of mathematics and physics in chemistry, and in this direction anticipated many of the points of view of the later nineteenth century. Lomonossoff's unfinished treatise, "The Elements of Mathematical Chemistry" (1741), of which only a fragment survives, deals with a conception which, in all his writings, he never ceased to urge, namely, the value of mathematical methods in chemistry. Ten years later, in an "Address on the Uses of Chemistry" (1751), he speaks as follows:

"If chemistry unites to solid form the separated and scattered particles in a solution, and brings forth various formations, it must be that she relies upon the strictest and most highly developed Geometry. If she changes solids into liquids and liquids into solids, and divides and unites them to give various substances, it must be that she seeks counsel of the most exact and ingenious Mechanics. If chemistry, by union of different substances, gives rise to different colors, she needs the help of the most profound optics. If the knowledge-seeking, tireless investigator [in response to this] will only survey her through geometry measure her forces by mechanics, and consider her through the science of optics, he will probably reach his desired goal." In this we seem to see at least an adumbration of chemical crystallography, and of chemical dynamics and statics. He continues: "Why have investigators had no success? I answer that for this a very skilful chemist is needed, who

is at the same time a mathematician." Has not the recent development of the science been along the precise lines which he thus lays down?

Lomonossoff's applications of geometry in *De Nitro* (1749), a comprehensive study of saltpeter, will illustrate his own attempts to use mathematical methods. He discusses at length the crystalline form of the substance and proceeds to develop theory of crystalline structure. In saltpeter, the prismatic form can be accounted for by an arrangement of round particles, in such a way that lines drawn through their centers always form equilateral triangles. In other substances, the arrangement is different, so that, for example, in common salt, the lines through the particles may form squares. As usual, he paid the penalty of being far ahead of his time. Yet he had anticipated by a century the essential conceptions of Bravais (1850), whose mathematical study of all possible space nets, and their relation to existing crystalline forms, coming at a more favorable time, led almost immediately to the completion of development along this line by Sohncke (1867).

In the same address, he continues: "[The chemist] is surely unapt, who has made a mass of experiments, but in the effort to secure quickly accessible products, hastens to the attainment of this as his sole goal; he overlooks those phenomena and changes occurring in his operations which might lead to the explanation of nature's secrets." If this viewpoint, with its contempt for purely preparative chemistry, had been as prominent in the creed of all the chemists of the century and a half since Lomonossoff's time, as it was in his own, instead of being until recently the ideal of only a few scattered chemists, what a different science ours would have been! How many papers, signed by notable names, might have offered something of substantial scientific value, in place of a mass of new entries for the indexes of Beilstein and Dammer! In the preface to his treatise on saltpeter, he develops the same idea: "Since as yet no general physical bases for explaining the formation and composition of chemical substances exist, and since few physical experiments have been applied in chemistry so as to lead to the desired results, it may seem difficult, but we believe it to be possible, scientifically, to describe the greater part of chemistry in terms of the interrelations of its own principles, and their connections with those of physics. We do not doubt that, after the union of chemical with physical truths, we shall be able more successfully to understand the inner nature of substances." Be it understood, these generalities are only summaries of the plans of study which, in his experimental work and in his papers, he attempts in thoroughgoing fashion to put into practice. Uttered as they were in the heart of the period of phlogiston, of heat-matter, and of confused experimentation and reasoning, they have an uncanny sound, and almost terrify us with their supernatural prescience. How long have we had to await

the psychological moment for the general application of these ideas! Had only the times been ripe; had only the atmosphere been healthy for the propagation of such ideas as his, instead of being virulently poisonous to them, our science might easily, by now, have been a hundred years ahead of its present position, and we might to-day have been listening to papers which, as it is, will not be read for a century. If Dante's *Divina Commedia* were to be revised by a chemist and brought up to date, the chief change he would make would be the provision of some horrible and revolting torment, calculated to give Stahl his just deserts.

The occasion is not a suitable one for going in detail into the mass of (for that time) novel and suggestive quantitative physico-chemical experiments which occupied Lomonossoff from 1752 to 1756. The extent of his plans—only partially fulfilled—may be judged from his *Dromus ad veram chymiam physicam* (Course in True Physical Chemistry, 1752), of which a considerable part was written, and much survives. In the introduction he mentions, among other aims of physical chemistry, this: "One must determine the specific properties of every substance as exactly as possible, in order that, after the composition has been ascertained by chemical operations, one may judge whether, and to what extent each property is altered by changing a given constituent." No statement of one of the purposes of physical chemistry could be clearer.

In the experimental part of the book, salt solutions receive much attention, and many modern problems may be recognized, such as measurement of exact solubilities at various temperatures, volume changes in solution, heats of solution, boiling points of solutions, relative cohesion in water and in solutions, capillary phenomena, action of electricity upon solutions, and relative deliquescent tendencies of salts. There is, of course, a good deal about crystallography. In the absence of the laboratory note-books, only parts of some of the tabulated results have been found. One set of experiments, chiefly with common salt, led to the conclusion that the freezing points of solutions are lower in proportion to the amount of the dissolved body. Even the most insignificant experiments were carried out quantitatively.

In Lomonossoff's laboratory, a good deal of special apparatus was devised. Measurements of the coefficient of expansion of air had been made, and a value (recalculated to 1°C.) of 0.003 (in place of 0.00367) was found. This led to the construction of an air thermometer for measuring low temperatures. Incidentally, he reformed the Delisle scale of temperatures, which ran downwards from 0° at the boiling point of water to 150° at the freezing point, by simply inverting it ($0^{\circ}\text{L.} = 0^{\circ}\text{C.}$, $150^{\circ}\text{L.} = 100^{\circ}\text{C.}$). A thermostat for ice and water was employed in some experiments, and instruments for the study of oceanography, devised by him, came afterwards into general use. One of the most extensive pieces

of work done in his laboratory was a study of colored glasses and mosaics, the results of which led to the establishment of a factory, still in successful operation, near St. Petersburg.

The achievements of Lomonossoff outside of chemistry were as remarkable as those within that science. He wrote a treatise on Metallurgy, made investigations in Meteorology and especially atmospheric electricity, in Geology, and in Mineralogy, and he superintended the equipment of expeditions for geographical exploration. He observed the transit of Venus of 1761, and drew from his observations the conclusion that the planet had an atmosphere "similar to, or perhaps greater than that of the earth," a discovery generally attributed to Schröter and Herschel (1791).

No undertaking that required courage and originality was outside the comprehensive sphere of his interests. He was the first to attempt to apply modern forms to the writing of poetry in the Russian language, and was the author of odes, poems, and even of tragedies to be performed in the Court Theater. He prepared a Russian grammar and a treatise on rhetoric. He devised a vocabulary for expressing scientific conceptions, and his terms are those now in use in Russia. As the most prominent Russian man of science of his time, public affairs claimed much of his strength. Taking him all in all, the rediscovery of Lomonossoff has added at once a chemist of the first magnitude and a personality of marvelous force and range to the limited gallery of the World's very greatest men.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 79.]

THE POTENTIAL OF THE POTASSIUM ELECTRODE.

BY GILBERT N. LEWIS AND FRÉDÉRIC G. KEYES.

Received November 29, 1911.

The method employed by Lewis and Kraus¹ for the determination of the potential of the sodium electrode is applicable in a number of similar cases. We shall describe in this paper a similar determination of the potential of the potassium electrode, together with some preliminary experiments carried out for the purpose of seeing how far the same method is available in the case of lithium, rubidium, caesium and the metals of the alkaline earths.

We first determined the potential of a dilute potassium amalgam in an aqueous solution of potassium hydroxide, against a normal calomel electrode, and thus were able to calculate the potential of this potassium amalgam against a normal solution of potassium ion in water. It remained to determine the difference in potential between this amalgam of potassium and pure metallic potassium. This difference of potential

¹ THIS JOURNAL, 32, 1459 (1910).

is measured by the electromotive force of a cell with electrodes of pure potassium and this potassium amalgam, and with a suitable electrolyte. Any electrolyte will serve which contains potassium salt and remains unattacked by the electrodes. A solution of potassium iodide in liquid ethylamine fulfils these conditions.

The apparatus for preparing and storing the amalgam and the anhydrous ethylamine has been described in the preceding paper. The cell was made and filled substantially as before. The vessel in which the potential of the amalgam was measured against the normal electrode was somewhat modified, as described in the following section.

Electrode Potential of 0.2216 per cent. Potassium Amalgam.

The apparatus here used is shown in Fig. 1. The amalgam was admitted to the electrode E from the reservoir A through the stopcock S. The electrode chamber was filled through K with a solution of potassium hydroxide of concentration 0.2026 *N*, which, moreover, completely filled the connecting tube C. The tube I contained the intermediate liquid 0.2 *N* KCl, and into this also dipped the end of a normal electrode, B, of the form commonly used in this laboratory.

The electromotive force of this combination at first was 2.1892 volts, but changed slowly on standing. A little more amalgam was admitted to E, effecting a removal of the electrode surface. Since this forced a certain amount of the hydroxide into the intermediate solution, the latter was also renewed. The electromotive force then returned to the initial value. This process of renewal was repeated many times and frequently the potassium hydroxide in the electrode chamber was also renewed through K. On standing, the e. m. f. usually diminished at the rate of 2–3 millivolts per hour, owing to small changes in concentration occurring at the surface of the amalgam electrode. On renewing the surface the e. m. f. almost always returned to the value 2.1890 or 2.1891, although occasionally it deviated from this value by several tenths of a millivolt. As a final value we have chosen 2.1891.

This value includes the two liquid potentials 0.2 *N* KOH–0.2 *N* KCl, and 0.2 *N* KCl–*N* KCl. The latter potential we will neglect. We have taken for the former the value 0.0169 from the work of Lewis and Sargent.¹ This potential is in such a direction that the total e. m. f. exclusive of liquid potentials is $2.1891 + 0.0169 = 2.2060$. Assuming the degree

¹ THIS JOURNAL, 31, 367 (1909).

of dissociation to be 0.83, the concentration of potassium ion in the 0.2026 *N* potassium hydroxide would be 0.1681 *N*. By means then of the Nernst equation we find for the potential of the dilute potassium amalgam against normal potassium ion, 2.1603 volts at 25°, the potential of the normal electrode being taken as zero.

Difference in Electrode Potential between Potassium and the Potassium Amalgam.

The first cell with electrodes of potassium and potassium amalgam, and with an electrolyte consisting of a solution of potassium iodide in liquid ethylamine, was set up during the course of the preceding investigation. The cell was found less satisfactory than the corresponding sodium cell. In the first place, owing to the much smaller solubility of potassium iodide, the potentiometer was much less sensitive. Moreover, the solid metal appeared to be attacked by the amine solution. This is extraordinary, as we have since sealed up potassium with ethylamine and heated to 70–80° without any observable reaction, and even after standing for some months the metal retained its bright untarnished luster, while the liquid above the metal showed no measurable electrical conductivity.

Nevertheless, in this first cell, a blue color, due doubtless to solution of the metal, appeared near the potassium electrode. In the course of several days loose particles of metal, which had obviously come from a kind of disintegration of the potassium electrode, were seen floating about in the solution. However, during the first day or two it was possible to obtain fairly satisfactory values of the e. m. f. when the contents of the cell were thoroughly stirred. These values varied between 1.0475 and 1.0485, the mean being 1.0480.

The solution which had remained for more than a year in contact with metal and amalgam in this cell we decanted into a new cell with fresh electrodes, suitable precautions being taken to avoid the entrance of air or moisture. The electromotive force of this cell varied over an extreme range of 0.0006 volt, the mean value of the e. m. f. being 1.0482. A third cell, containing fresh materials throughout, gave an e. m. f. varying through a range of 0.0008 volt, with a mean of 1.0481. This value, 1.0481 volts, may be taken as the mean of the three cells. In order now to obtain the electrode potential of solid potassium against a normal solution of potassium ion in water, it is only necessary to add this value to the electrode potential of the potassium amalgam, namely, $2.1603 + 1.0481 =$ 3.2084 volts.

The Heat of Solution of Potassium in Mercury; Experiments on Other Metals.

The temperature coefficient of the e. m. f. of the cell with potassium and potassium amalgam electrodes was measured between 25° and 0°

and found to be -0.000272 volt per degree. We may therefore determine the heat of solution of potassium in 0.2216% potassium amalgam with the aid of the Gibbs-Helmholtz equation,

$$E - Q/F = T dE/dT,$$

where Q is the heat evolved in the solution of one equivalent of potassium in a large quantity of 0.2216% amalgam, and F is the Faraday equivalent. Using the same values of F and the mechanical equivalent of heat as in the preceding paper, we find Q equal to 109060 joules or 26050 cal.

Experiments are in progress to determine how far the method used for the electrode potential of sodium and potassium is applicable to other metals of the alkalis and alkaline earths. Lithium is soluble in ethylamine and it has therefore been necessary to prepare for this purpose dry propylamine in which lithium iodide proves to be readily soluble. In the case of rubidium and caesium a serious difficulty has been encountered, due to the fact that their iodides are practically insoluble in ethylamine. It will therefore be necessary in these cases to choose another type of solvent or of salt. The iodides of calcium, strontium and barium are soluble in ethylamine, the solubility diminishing in the order given.¹ Therefore the problem consists in obtaining the metals in a state of sufficient purity, and in devising a method of introducing them into the cell, for on account of their high melting point the method hitherto employed is impossible.

Summary.

The potential of potassium in a normal solution of potassium ion at 25° is found to be 3.2084 volts against the normal calomel electrode taken as zero.

This is the sum of two values: (1) 2.1603 volts, the potential of 0.2216% potassium amalgam against normal potassium ion, and (2) 1.0481 volts, the difference in potential between potassium and 0.2216% potassium amalgam in a solution of potassium iodide in ethylamine.

The temperature coefficient of the latter electromotive force is -0.000272 volt per degree; hence the heat of solution of potassium in mercury is 26050 cal.

We wish to express our indebtedness to the Bache fund of the National Academy for financial aid in prosecuting this investigation.

¹ An interesting phenomenon has been observed in the case of several of the iodides when treated with ethylamine. The dry salt dissolves until a definite concentration (as measured by conductivity) is reached. The solubility then remains constant for some hours until a new voluminous solid phase appears which undoubtedly contains ethylamine of crystallization. In the case of calcium iodide the swelling of the solid, due to the formation of this new phase, was so considerable as to burst the containing tube.

THE HYDROLYSIS OF SODIUM OXALATE AND ITS INFLUENCE UPON THE TEST FOR NEUTRALITY.¹

BY WILLIAM BLUM.

Received November 29, 1911.

I. Introduction: 1. Purpose of the Investigation. 2. Sources of Uncertainty in Sørensen's Method. II. Hydrolysis of Sodium Oxalate: 1. Theoretical Considerations: (a) Calculation of the Theoretical Hydrolysis; (b) Calculation of Standards for Comparison; (c) Choice of Indicator for Comparison. 2. Experimental Part: (a) Purification and Preparation of Materials and Solutions; (b) Stability of Sodium Oxalate Solutions; (c) Effect of Sodium Oxalate Solution on Glass; (d) Presence of Sodium Bicarbonate in Sodium Oxalate; (e) Colorimetric Comparisons. 3. Conclusions from the Comparisons. 4. Discussion of Discrepancies. III. Determination of Excess Alkali or Acid in Sodium Oxalate: 1. Error Caused by Neglecting Hydrolysis. 2. Calculation of Impurities Present. 3. Effect of Impurities on Standardizing Value. IV. Summary.

I. Introduction.

1. *Purpose of the Investigation.*—The use of sodium oxalate as a primary standard for acidimetry and oxidimetry was suggested in 1897 by Sørensen,² who described its preparation, testing and use, in subsequent papers.³ Its general adoption as a standard has been hindered by the difficulty of securing from the manufacturers material of a purity conforming to the specifications prepared by Sørensen.⁴ In order to determine the composition of sodium oxalate as purchased, and to secure, if possible, a material of the requisite purity to issue as a standard sample, specimens of sodium oxalate were obtained by purchase in the open market or directly from the maker, from two European and three American manufacturers. In the course of the subsequent tests, the methods described by Sørensen were found satisfactory, with the exception of that for the determination of sodium carbonate or sodium acid oxalate, in which discrepancies were found, which led to the following investigation. Sørensen's directions are given in the following paragraph, and an improved method, based on this investigation, is described in the final summary:

2. *Sources of Uncertainty in Sørensen's Method.*—Sørensen's method for testing the neutrality of the sodium oxalate is as follows: Introduce into a conical Jena flask about 250 cc. of water and 10 drops of phenolphthalein solution (0.5 gram phenolphthalein dissolved in 50 cc. alcohol and 50 cc. of water), and evaporate to 180 cc. while passing in a current of pure air, free from carbon dioxide. Allow to cool to the ordinary temperature and add 5 grams of sodium oxalate. Upon shaking carefully, while maintaining the current of air, the oxalate slowly dissolves. If the solution is red, not more than 4 drops of decinormal acid should

¹ Published by permission of the Director of the Bureau of Standards.

² *Z. anal. Chem.*, 36, 639-43 (1897).

³ *Ibid.*, 42, 333-59, 512-6 (1903).

⁴ Merck, "Prüfung der Chemischen Reagenzien auf Reinheit," (1905); Krauch-Merck, "Chemical Reagents," (1907).

be required to render it colorless, while if the solution is colorless, it should acquire a distinct red color upon the addition of not more than 2 drops of decinormal sodium hydroxide.

Preliminary experiments showed that the following points in the above method required investigation:

(a) Is pure sodium oxalate neutral toward phenolphthalein, or is the hydrolysis sufficient to produce an alkaline reaction?

(b) Does sodium oxalate solution decompose on boiling, or is the increased alkalinity due to the action upon the glass?

(c) Is any excess of alkali present entirely in the form of Na_2CO_3 , or may NaHCO_3 actually exist in a material heated to 240° ?

(d) Under given conditions of titration, to what form should the excess of alkali or acid be calculated, and what errors in the use of sodium oxalate as an acidimetric or oxidimetric standard are caused by the presence of a given excess of acid or alkali?

II. The Hydrolysis of Sodium Oxalate.

1. *Theoretical Considerations.*—Souchay and Lenssen¹ stated that "the aqueous solution does not affect curcuma paper, but blues red litmus paper, especially on boiling." Sørensen² considered that the slightly alkaline reaction which most of his preparations showed toward phenolphthalein was probably due to a trace of sodium carbonate, though admitting the possibility of alkalinity due to hydrolysis, in the sense of the equation

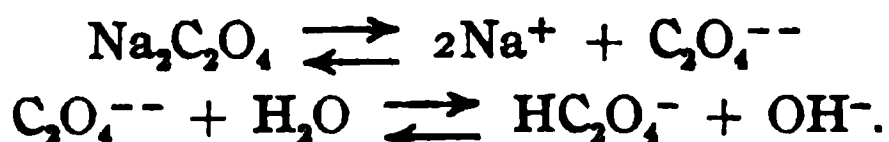


Since the apparent alkalinity of his samples (a maximum of about 0.05% Na_2CO_3) represented a negligible error when used as an acidimetric standard, Sørensen dismissed the subject without further study.

(a) *Calculation of the Theoretical Hydrolysis.*—The hydrolysis of sodium oxalate may be represented thus:



which may be expressed as follows in terms of ions:



The hydrolysis may be considered as due entirely to the small value of the ionization constant of the second hydrogen of oxalic acid, which is only about one-thousandth of that of the first hydrogen of this acid.³ In such a solution, therefore, $[\text{HC}_2\text{O}_4^-]$ is practically equal to $[\text{OH}^-]$, while $[\text{C}_2\text{O}_4^{--}]$ is equal to the product of the concentration of the salt and its ionization. Thus:

¹ *Ann.*, 99, 33 (1856).

² *Z. anal. Chem.*, 42, 351 (1903).

³ Chandler, *THIS JOURNAL*, 30, 694-713 (1908).

$$[\text{HC}_2\text{O}_4^-] = [\text{OH}^-] \quad K_{A_2} = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{--}]}{[\text{HC}_2\text{O}_4^-]}$$

$$[\text{C}_2\text{O}_4^{--}] = \gamma C \quad K_w = [\text{H}^+][\text{OH}^-]$$

where c = molar concentration of the solution, i. e., the number of gram molecules in one liter of the solution.

γ = ionization of the salt.

K_{A_2} = dissociation constant for the second H of $\text{H}_2\text{C}_2\text{O}_4$.

K_w = dissociation constant for H_2O .

By substitution $[\text{H}^+] = \sqrt{K_{A_2}K_w/\gamma C}$.

To calculate $[\text{H}^+]$ for 0.1 M (molar) solution of sodium oxalate, the following values were employed:

$$K_{A_2} = 4.5 \times 10^{-5}, *$$

$$K_{w_{25^\circ}} = 1.1 \times 10^{-14} \text{ and } K_{w_{18^\circ}} = 0.6 \times 10^{-14}. \dagger$$

$$\gamma = 0.7. \dagger$$

		Round number employed.
from which	$[\text{H}^+]_{18^\circ} = 1.96 \times 10^{-9}$	2.0×10^{-9}
and	$[\text{OH}^-]_{18^\circ} = 3.06 \times 10^{-6}$	3.1×10^{-6}
	$[\text{H}^+]_{25^\circ} = 2.66 \times 10^{-9}$	2.7×10^{-9}
	$[\text{OH}^-]_{25^\circ} = 4.14 \times 10^{-6}$	4.1×10^{-6}

In the subsequent calculations the round numbers indicated have been employed.

(b) *Calculation of Standards for Comparison.*—For the purpose of comparison, standards of calculated alkalinity were prepared from mixtures of ammonium chloride and hydroxide, on the following basis:

* Chandler [THIS JOURNAL, 30, 694-713 (1908)] found by partition experiments 4.1×10^{-5} , and by conductivity, 4.9×10^{-5} . The mean value 4.5×10^{-5} has been employed for both 18° and 25° , although determined by Chandler at 25° ; since the temperature coefficient is probably less than the uncertainty in the value for 25° .

† Derived from the following values:

	25° , $K \times 10^{14}$.	18° , $K \times 10^{14}$.
Arrhenius, <i>Z. physik. Chem.</i> , 11, 805 (1893)...	1.2	..
Wijs & van't Hoff, <i>Ibid.</i> , 12, 514 (1893)	1.4	0.64
Löwenherz, <i>Ibid.</i> , 20, 283 (1896)	1.4	..
Kanolt, THIS JOURNAL, 29, 1402 (1907)	0.8	0.46
Hudson, <i>Ibid.</i> , 31, 1130 (1909)	1.0	..
Lorenz & Böhi, <i>Z. physik. Chem.</i> , 66, 733 (1909)	1.2	0.72
Heydweiller, <i>Ann. Physik</i> , 28, 503 (1909)	1.0	0.59
[Recalc. from Kohlrausch & Heydweiller, <i>Wied.</i> <i>Ann.</i> , 53, 709 (1894)]	—	—
Mean,	1.1	0.60

† Kohlrausch [*Leitvermögen der Elektrolyte*, p. 161 (1898)] and Noyes and Johnston [THIS JOURNAL, 31, 987 (1909)], both found for 0.1 M $\text{K}_2\text{C}_2\text{O}_4$ at 18° , $\gamma = 0.7$, which value has been assumed to hold for $\text{Na}_2\text{C}_2\text{O}_4$.

The ionization constant¹ of ammonium hydroxide at 25° = 1.8×10^{-5} , *i. e.*,

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.8 \times 10^{-5} \text{ and } \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{1.8 \times 10^{-5}}{[\text{OH}^-]}$$

$$\therefore \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{1.8 \times 10^{-5}}{4.1 \times 10^{-6}} = 4.4$$

Since, however, 0.1 *N* NH_4Cl is about 85% ionized² it is necessary to use $4.4 \div 0.85 = 5.2$ parts of 0.1 *N* NH_4Cl to 1 part 0.1 *N* NH_4OH to prepare a solution in which $[\text{H}^+]_{25^\circ} = 2.7 \times 10^{-9}$.

A second comparison was made with 0.1 *N* sodium acetate, for which the following constants were employed:

$$K_{\text{Ac}} = 1.8 \times 10^{-5},^*$$

$$\gamma = 0.8$$

from which

$$[\text{H}^+] = \sqrt{K_{\text{Ac}}K_w/\gamma C} = 1.6 \times 10^{-9},$$

i. e., 0.1 *N* sodium acetate should be slightly more alkaline than 0.1 *M* sodium oxalate.

Mixtures of 0.1 *N* sodium borate and hydrochloric acid, and of glycocoll and sodium hydroxide were also prepared, according to Sørensen³ who calculated $[\text{H}^+]_{18^\circ}$ for such solutions from e. m. f. measurements with a hydrogen electrode.⁴ As his measurements were made at 18°, the observations were confined to that temperature.

(c) *Choice of Indicator for Comparison.*—Preliminary tests showed that phenolphthalein is the only indicator that is sensitive in solutions of exactly this alkalinity. Alizarin, cyanin and dinitrohydroquinone all proved unsatisfactory for accurate matching, though the latter was sufficiently sensitive to confirm approximately the results with phenolphthalein. The indicator selected for the final comparison was, therefore, phenolphthalein, for which the most probable value⁵ of *K* is 1.7×10^{-10} . In a solution in which $[\text{H}^+]_{25^\circ} = 2.7 \times 10^{-9}$ this indicator should, therefore, be transformed into its salt to the extent of 5.9%.⁶

$$\frac{[\text{H}^+][\text{I}^-]}{[\text{HI}]} = 1.7 \times 10^{-10}$$

¹ Noyes and Sosman, "Electrical Conductivity of Aqueous Solutions," *Carn. Inst. Pub.*, 63, 228 (1908).

² Calculated from Kohlrausch, "Leitvermögen der Elektrolyte," p. 159 (1898).

³ Noyes and Sosman, *loc. cit.*

⁴ Sørensen, *Compt. rend. trav. lab. Carlsberg*, 8, 1-168 (1910); *Biochem. Z.*, 21, 131-304 (1910).

⁵ Several of Sørensen's mixtures were checked electrometrically and colorimetrically by Auerbach and Pick, *Arbeit. Kais. Gesundheitsamte*, 38, 243-74 (1911).

⁶ Hildebrand, *Z. Elektrochem.*, 14, 351 (1908). Wegscheider, *Ibid.*, 510 (1908). Rosenstein (Mass. Inst. Tech.), private communication from W. C. Bray.

⁶ Noyes, *THIS JOURNAL*, 32, 861 (1910).

$$\frac{[\text{I}^-]}{[\text{HI}]} = \frac{1.7 \times 10^{-10}}{2.7 \times 10^{-9}} = 6.3 \times 10^{-2} = \frac{5.9}{94.1}$$

These calculations are based upon the assumption that the ionization constant of phenolphthalein is the same at 18° and 25° and that the color of the indicator is not materially affected by the presence of neutral salts.

2. Experimental Part.

(a) Purification and Preparation of Materials and Solutions.

Air.—Air was freed from carbon dioxide by passage through two wash bottles containing 30% potassium hydroxide and a U tube with a ten-inch column of soda lime, followed by absorbent cotton.

Water.—The regular distilled water was re-distilled from alkaline permanganate. It was then boiled in a seasoned Jena flask for two hours in a stream of pure air and preserved in a Jena flask provided with a siphon and a soda lime guard tube. This water has a specific conductivity of 2×10^{-6} reciprocal ohms and evolved no carbon dioxide when a small portion was boiled for one-half hour in a stream of pure air, which after being dried with calcium chloride was passed through a weighed soda lime tube.

Sodium Oxalate.—Pure sodium oxalate was prepared from two commercial samples. One, designated A, contained originally (as determined in the final tests) 0.02% NaHC_2O_4 , while that marked B contained 0.04% Na_2CO_3 and considerable CaC_2O_4 . These materials were recrystallized in platinum, the solutions being electrically heated, and the surrounding atmosphere being kept as free from carbon dioxide as possible. The fine crystals obtained were sucked dry on a platinum cone, and dried in an electric oven at 240°. A portion of the product of the third recrystallization of B was dissolved in water and precipitated by the addition of double distilled neutral alcohol, the product being filtered out and dried as above. The following samples of sodium oxalate were thus obtained:

Water crystallization, $A_1, A_2; B_1, B_2, B_3$.

Alcohol precipitation B_4 .

Since in subsequent tests these samples were found to produce almost the same colors with phenolphthalein, we may conclude that a single water crystallization eliminated practically all of the impurities above noted, and as a constant and uniform product was obtained by recrystallization of materials originally respectively acid and alkaline, it is reasonably certain that the product represented pure sodium oxalate.

Ammonium Chloride.—A normal solution was prepared from J. T. Baker's special ammonium chloride, dried at 110° for two hours. This material was found to contain no organic bases when tested according to Krauch.

Ammonium Hydroxide.—A decinormal solution was prepared from re-distilled ammonia and standardized against decinormal hydrochloric acid, which in turn was standardized gravimetrically by means of silver chloride. Methyl red was used as the indicator. The solution was preserved in a ceresin-lined bottle and measured in a burette closed with a soda lime tube.

Sodium Hydroxide.—Pure material was prepared from metallic sodium with exclusion of carbon dioxide.¹ The resulting strong solution was titrated against standard hydrochloric acid and diluted to 0.01 *N* solution, which was preserved in a ceresin-lined bottle.

Oxalic Acid.—A 0.01 *N* solution was prepared from J. T. Baker's crystallized oxalic acid.

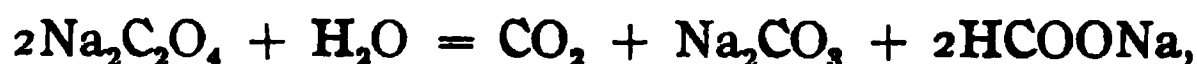
Sodium Acetate.—Merck's crystallized sodium acetate was recrystallized in platinum. The products of the crystallizations were sucked dry on a platinum cone, dried between filter paper and finally air-dried.

Sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) solution was prepared from equivalent quantities of twice recrystallized boric acid, and pure sodium hydroxide.

Glycocoll (amino-acetic acid) solution was prepared according to Sørensen, by dissolving 7.505 grams glycocoll (Kahlbaum) and 5.85 grams NaCl in one liter.

Phenolphthalein.—A 1% alcoholic solution of the indicator was employed *i. e.*, about 0.03 *N*. In each comparison exactly 0.2 cc. of this solution was employed in a total volume of 150 cc., thus giving a solution in which the phenolphthalein is about 1/22000 *N*. According to McCoy,² the saturated aqueous solution of this indicator is about 1/11000 *N*. A solution of such concentration (*i. e.*, 0.4 cc. in 150 cc.) was, however, always turbid, so that the smaller concentration was employed, giving a color of convenient intensity for comparison. Alcohol was not present in amount sufficient to affect the color³ of the indicator.

(b) *Stability of Sodium Oxalate Solutions.*—Before attempting to prepare and test pure sodium oxalate, it was necessary to determine the effect of heat upon its solution. Sørensen⁴ found that a sodium oxalate solution became more alkaline upon boiling, whether in water that had previously been boiled or not, and equally in a stream of air, oxygen or nitrogen. He attributed the increased alkalinity to a decomposition in the sense of the equation



¹ Findlay, "Practical Physical Chemistry," p. 176 (1906).

² *Am. Chem. J.*, 31, 503 (1904).

³ McCoy, *Ibid.*, 31, 503 (1904). Hildebrand, *Z. Elektrochem.*, 14, 351 (1908). *THIS JOURNAL*, 30, 1914 (1908).

⁴ *Z. anal. Chem.*, 42, 352 (1903).

quoting Carles¹ who found that oxalic acid solution decomposed similarly if boiled in a stream of an inert gas.

That no appreciable decomposition takes place upon boiling sodium oxalate solution was shown by the following experiments:

Five grams of the salt were boiled with pure water in a stream of pure air, which was passed through calcium chloride and then through a weighed soda lime tube. The latter was reweighed at the end of two hours, replaced, and the solution acidified and again boiled to determine whether any sodium carbonate was formed in the boiling of the aqueous solution. The amount of carbon dioxide evolved on direct acidification was also determined. The apparatus and method were tested with known small quantities of sodium carbonate.

TABLE I.—EVOLUTION OF CARBON DIOXIDE ON BOILING SOLUTIONS CONTAINING FIVE GRAMS OF SODIUM OXALATE.

Exper.	Sample.	Solution.	Time. Minutes.	Weight of CO ₂ . Mg.
1	A	Acidified	15	0.3
2a	A	Aqueous	15	0.0
b	A	Aqueous	+ 120	0.2
c	A	Acidified	+ 15	0.2
3a	B	Acidified	15	1.3
b	B	Acidified	30	1.4
4a	B	Aqueous	15	0.6
b	B	Aqueous	+ 120	0.3
c	B	Acidified	+ 15	0.5

Since in experiments 1 and 2b practically the same amount of CO₂ was evolved on 15 minutes' treatment with acid as upon two hours' boiling with water, we may conclude that no appreciable decomposition takes place in two hours' boiling, though the solutions become markedly alkaline. The evolution of 0.6 mg. CO₂ in 4a is believed to be due to the presence of NaHCO₃ (or occluded CO₂) in this sample (p. 127).

(c) *Effect of Sodium Oxalate Solution on Glass.* — Further tests showed that there was no increase in alkalinity upon boiling the sodium oxalate solution for two hours in a platinum dish or in a quartz flask in a current of pure air (cf. Table II, 1b,c,d). The increased alkalinity noted by Sørensen must, therefore, have been due to the attack of the glass (Jena glass) employed by him. Since it was impracticable to employ entirely quartz flasks, tests were carried out to determine the relative effect of sodium oxalate solutions upon different kinds of glass. Flasks of several kinds of glass were prepared of approximately the same shape and size, with tubes ground in for the inlet and exit of the pure air (except the quartz flask). Two-gram portions of sodium oxalate were boiled with 125 cc. pure water and 0.2 cc. phenol-

¹ *Compt. rend.*, 71, 226 (1870).

phthalein solution in a stream of pure air. At the end of the test they were titrated with 0.01 *N* oxalic acid till the solutions were colorless. The results were as follows:

TABLE II.—EFFECT OF SODIUM OXALATE SOLUTIONS UPON GLASS. INCREASED ALKALINITY IN TERMS OF 0.01 *N* OXALIC ACID.

Expt.	Glass.	Sodium oxalate.	Time. Min.	Volume of 0.01 <i>N</i> $H_2C_2O_4$. cc.
1a	Quartz	A	120	0.0
b	Quartz	F	120	0.5 ¹
c	Quartz	F	60	0.5
d	Quartz	F	10	0.4
2a	Durax	A	120	0.5
b	Durax	A	120	0.5
c	Durax	F	120	0.7
3a	Jena Geräte	A	120	4.9
b	Jena Geräte	A	120	4.6
c	Jena Geräte	F	120	5.1
4a	German soft	A	120	6.8
b	German soft	A	120	6.7
c	German soft	F	120	6.5
5a	Resistance	A	120	8.7
b	Resistance	A	120	6.6
c	Resistance	F	120	8.5
6a	Jena Verbund	F	120	4.1

From Table II it is evident that the Durax glass² is not appreciably attacked by neutral or faintly alkaline sodium oxalate solutions during two hours' boiling, *i. e.*, much longer than is required to expel any CO_2 from the solution. For the subsequent experiments, vessels of quartz, platinum, or Durax glass were, therefore, employed. It may be noted that in none of the flasks did the solution acquire more than a very faint pink color at the end of 15 minutes, though the Jena Geräte glass was most rapidly attacked, and is least suited for this purpose. As the successive tests of each glass were made on the same vessels with approximately equal results there is no marked evidence of "seasoning" of the glass by several hours' boiling.

(d) *Presence of Sodium Bicarbonate in Sodium Oxalate.*—Sørensen dismissed the question of the existence of sodium bicarbonate by stating that it could not possibly be present in material dried at 240° , since it decomposes at or below 100° . In the course of the testing, however, it was found that several of the samples when dissolved in pure water

¹ All the 2-hour results for F have been corrected for this "original" alkalinity.

² Durax glass made by Schott & Gen. is furnished only in the form of tubing, which formerly was distinguished by a longitudinal blue line, which has recently been changed to a green line. Verbund glass, formerly made with no distinguishing mark, now has a blue line. This information was secured directly from the maker, and is of importance in view of the confusion of terms in some of the recent catalogues of glassware.

containing phenolphthalein were colorless, or nearly so, but after a few minutes' boiling became strongly pink and remained pink on cooling, indicating the presence of an appreciable excess of alkali, which would have been overlooked if tested according to Sørensen. Such samples, e. g., B, evolved carbon dioxide upon boiling the aqueous solution, and upon boiling with acid evolved a total amount of carbon dioxide greater than would correspond to the titrated alkalinity, if calculated as Na_2CO_3 . From Table III it may be seen that in every case the gravimetric and volumetric results agreed more closely if calculated to NaHCO_3 than to Na_2CO_3 , and that in all but E, the carbon dioxide is apparently even in excess of that calculated for NaHCO_3 .

TABLE III.—DETERMINATION OF EXCESS ALKALI IN SODIUM OXALATE.

Expt.	Sample.	Grav. detn. of CO_2 . Calculated as		Vol. detn. of alkali. Calculated as	
		Na_2CO_3 . %	NaHCO_3 . %	Na_2CO_3 . %	NaHCO_3 . %
1	B	0.065	0.051	0.036	0.057
2	C	0.291	0.230	0.107	0.171
3	D	0.308	0.244	0.120	0.192
4	E	1.31	1.05	0.70	1.11

It is evident, therefore, that if such samples were tested with the object of making corrections for accurate work, appreciable errors might arise if the alkalinity were calculated to Na_2CO_3 . For samples containing less impurity than B, the differences would be entirely negligible.

With our present means of analysis, it is impossible to state whether such "excess" carbon dioxide (above Na_2CO_3) is present as NaHCO_3 , or in some occluded form. That it is not readily given off at 240° was shown in E, which lost only 0.14% in two hours' heating at 240° , though it contained about 0.4% of such excess "carbonic acid." When we consider that as usually prepared (by neutralization of oxalic acid with sodium carbonate) the salt separates from a solution charged with carbon dioxide; it is not impossible that the latter should be occluded in it, in a form in which it is not readily expelled at high temperatures, just as water has been shown to exist in materials heated to high temperatures.¹

(e) *Colorimetric Comparisons*.—All of the solutions for comparison were prepared in 300 cc. flasks of Durax glass with a long, narrow neck to facilitate exclusion of carbon dioxide. Before being used, these were boiled for two hours with pure water, allowed to soak in water for 36 hours, and were filled with 0.1 M sodium oxalate (or solutions of approximately the same alkalinity) for several days before the final tests were made.

Decimolar solutions of sodium oxalate were prepared by dissolving two grams of the salt in 150 cc. of pure water, to which was added 0.2

¹ Richards, THIS JOURNAL, 33, 888 (1911).

cc. of phenolphthalein. The solutions were boiled for ten minutes in a stream of pure air, which was continued during their cooling to room temperature. The flasks were then closed with rubber stoppers and placed in a thermostat adjusted to the desired temperature ($\pm 0.2^\circ$).

Ammonium Chloride Hydroxide.—Solution of the calculated alkalinity ($[H^+]_{25^\circ} = 2.7 \times 10^{-9}$) was prepared by mixing 15.0 cc. *N* ammonium chloride, 28.8 cc. 0.1 *N* ammonium hydroxide and 0.2 cc. phenolphthalein and diluting to 150 cc., the resultant solution being decinormal with respect to the salt, *i. e.*, ammonium chloride. In the determinations of the value of the ionization constant for phenolphthalein given above, Hildebrand¹ and Rosenstein² employed solutions not over 0.05 *N*, with respect to ammonium chloride, in order to reduce the neutral salt effect.³ In these tests it was hoped that by making all the solutions 0.1 *N*, the neutral salt effect would be largely eliminated. (From the standpoint of hydrolysis, 0.1 *M* sodium oxalate may be considered as 0.1 *N*.)

From Sørensen's chart, mixtures of 7.06 cc. of 0.1 *N* $Na_2B_4O_7$ and 2.94 cc. 0.1 *N* HCl , or of 9.34 cc. glycoll solution and 0.66 cc. 0.1 *N* $NaOH$, produce solutions in which $[H^+]_{18^\circ} = 2.0 \times 10^{-9}$ (*i. e.*, $10^{-8.7}$). Mixtures in these proportions were prepared with a total volume of 150 cc.

Phenolphthalein solutions of calculated transformation were prepared⁴ by adding an accurately measured amount (0.2 cc.) of phenolphthalein to 150 cc. of water containing 10 cc. of 0.1 *N* sodium hydroxide, whereby the indicator was completely transformed into its red salt. Measured portions of this solution were then diluted to 150 cc. to produce the standards representing the desired percentage transformation. In each solution for comparison or titration, it is, of course, necessary to have exactly 0.2 cc. of the original phenolphthalein solution in the same total volume.

The following comparisons were made by direct optical matching of the solutions in the Durax flasks, which were all of the same shape and size. Attempts to use a colorimeter proved unsatisfactory, owing to the very light colors of the solutions and to very rapid fading of the sodium oxalate and acetate solutions upon exposure to air and even slight absorption of carbon dioxide. The results are expressed in percentage transformation of phenolphthalein, the standards for which did not vary appreciably in color between 18° and 25° .

¹ *Z. Elektrochem.*, 14, 351 (1908).

² Private communication from W. C. Bray.

³ Michaelis and Rona, *Z. Elektrochem.*, 14, 251–3 (1908); *Biochem. Z.*, 23, 61–7 (1909). Bohdan v. Szyszkowski, *Z. physik. Chem.*, 58, 420 (1907). Sørensen and Palitzsch, *Biochem. Z.*, 24, 387 (1910).

⁴ Noyes, *THIS JOURNAL*, 32, 826.

TABLE IV.—COLORIMETRIC COMPARISONS.

Expt.	Solution.	Composition or ratio.	Color. % transformation of phenolphthalein.			
			25°.		18°.	
			Calc.	Obs.	Calc.	Obs.
1	Na ₂ C ₂ O ₄ B ₁	0.1 M	5.9	3.5	7.8	4.0
2	Na ₂ C ₂ O ₄ B ₂	0.1 M	5.9	3.5	7.8	3.5
3	Na ₂ C ₂ O ₄ B ₃	0.1 M	5.9	4.0	7.8	4.0
4	Na ₂ C ₂ O ₄ B ₄	0.1 M	5.9	4.0	7.8	4.0
5	Na ₂ C ₂ O ₄ A ₁	0.1 M	5.9	4.0	7.8	4.0
6	Na ₂ C ₂ O ₄ A ₂	0.1 M	5.9	4.0	7.8	4.0
7	Na ₂ C ₂ O ₄ B ₁	0.2 M	7.8	6.0	10.2	6.0
8	NaC ₂ H ₃ O ₃	0.1 N	9.6	3.0	12.7	3.5
9	NaC ₂ H ₃ O ₃	0.1 N	9.6	3.0	12.7	3.5
10	{NH ₄ Cl NH ₄ OH	{5.2 1.0 }	5.9	6.5	9.8	8.5
11	{NH ₄ Cl NH ₄ OH	{6.7 1.0 }	7.8	5.0
12	{Na ₂ B ₄ O ₇ HCl	{7.06 2.94 }	7.8	5.5
13	{Na ₂ B ₄ O ₇ HCl	{6.84 3.16 }	6.8	4.0
14	{Glycocoll NaOH	{9.34 0.66 }	7.8	6.5
15	{Glycocoll NaOH	{9.52 1.48 }	5.9	4.0

3. *Conclusions from the Comparisons.*—From Table IV, the following conclusions may be reached:

a. The color produced by phenolphthalein in sodium oxalate solutions is not appreciably affected by changes in temperature between 18° and 25°.

b. As noted by Hildebrand¹ the colors produced in given mixtures of ammonium chloride and ammonium hydroxide are markedly affected by slight temperature changes, making such solutions unsuitable for practical comparison standards.

c. The colors produced in sodium acetate solutions² are far lighter than those calculated from the constants employed.

d. The color of the sodium oxalate solution is matched closely by solutions No. 13 and No. 15, in which, according to Sørensen's chart, $[H^+]_{18^\circ}$ is respectively 2.35×10^{-9} (or $10^{-8.63}$) and 2.7×10^{-9} (or $10^{-8.57}$). On the basis of Sørensen's e. m. f. measurements, $[H^+]_{18^\circ}$ for 0.1 M Na₂C₂O₄ may therefore be considered as equal to 2.5×10^{-9} (or $10^{-8.6}$); and $[OH^-]_{18^\circ}$ as equal to 2.4×10^{-9} (or $10^{-8.62}$). In other words the salt is hydrolyzed at 18° to the extent of 0.0024%.

¹ Z. Elektrochem., 14, 351 (1908).

² Salensky, Z. Elektrochem., 10, 204 (1904), found that N-NaC₂H₃O₃ solution was far less alkaline toward phenolphthalein than was indicated by calculation.

e. In all the solutions except No. 10, the colors with phenolphthalein are markedly less than those calculated from the ionization constant 1.7×10^{-10} .

4. *Discussion of Discrepancies.*—Extended discussion of the causes of the discrepancies between the various calculated and observed colors would be of little interest, owing to the uncertainties in the values of the constants employed, especially that of phenolphthalein.¹ The value accepted depends practically upon the ammonium chloride-hydroxide mixtures, used by Hildebrand and Rosenstein, since the individual values of Wegscheider are far from concordant. If the ionization constant of phenolphthalein were calculated from experiments 12 to 15, on the basis of Sørensen's e. m. f. measurements, the value $K = 1.1 \times 10^{-10}$ would be obtained, which agrees more closely with McCoy's value of 0.8×10^{-10} . Salm,² however, obtained the value $K = 8.0 \times 10^{-10}$ by measurements with the hydrogen electrode. The discrepancies in the present work are in accord with the results of Hildebrand, who found unexplainable irregularities in the value of K with less than 8% transformation. These discrepancies may be due to the fact that phenolphthalein acts as a dibasic acid, as shown by Acree³ and Wegscheider.⁴

In view of these uncertainties the reaction of pure sodium oxalate may best be defined empirically as equal to 4% phenolphthalein transformation in 0.1 *M* solution, and 6% in 0.2 *M* solution, standards which are readily reproducible and are free from any assumptions as to the value of the constants.

III. Determination of Excess Alkali or Acid in Sodium Oxalate.

1. *Error Caused by Neglecting Hydrolysis.*—Having shown that pure sodium oxalate (0.1 *M*) produces a pink color equivalent to 4% phenolphthalein transformation, accurate results in testing its neutrality will be obtained by titrating to such a standard color rather than to colorless. In order to determine the magnitude of such a correction, the following tests were made. Two gram samples of sodium oxalate dissolved as in the previous tests were titrated with 0.01 *N* oxalic acid or 0.01 *N* NaOH (a) to the standard color and (b) to colorless. The difference in the volume of 0.01 *N* acid or alkali required was always 0.3 cc., equivalent to 0.016% Na_2CO_3 , 0.025% NaHCO_3 , or 0.017% NaHC_2O_4 , on the assumption that in the cold the end point is reached when NaHCO_3 is formed. The error involved in titrating 4 g. in the same volume to colorless instead of the normal color for 0.2 *M* solution (6% phenolphthalein) is 0.6 cc., i. e., the percentage error is about the same. In general, therefore, any errors

¹ Noyes, *THIS JOURNAL*, 32, 859 (1910).

² *Z. Elektrochem.*, 10, 344 (1904).

³ *Am. Chem. J.*, 39, 528 (1908).

⁴ *Z. Elektrochem.*, 18, 510 (1908).

through titration to colorless are likely to be negligible, and far less than those caused by the presence of excess of carbon dioxide in the samples, or the attack of the glass during the boiling for its expulsion.

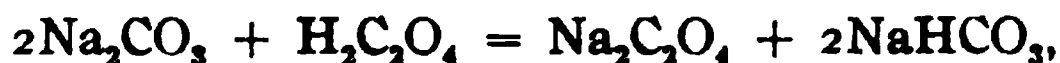
2. Calculation of Impurities Present.—The question as to the form in which the excess of alkali exists in a given sample cannot be determined without a detailed study of each sample. From the experience with numerous samples, most accurate results will probably be obtained by calculating the alkalinity to NaHCO_3 . In the case of samples containing less than 0.10% alkali, the differences will be negligible, *i. e.*, not over 0.04%. Samples containing much more than 0.10% of alkali are unsuitable for standardizing, even with a correction. Excess of acidity may be calculated as NaHC_2O_4 .

In the above calculations we have assumed that 1 cc. 0.01 *N* acid¹ is equivalent to 0.00106 g. Na_2CO_3 or 0.00168 g. NaHCO_3 , while 1 cc. 0.01 *N* NaOH is equivalent to 0.00112 g. NaHC_2O_4 , in accordance with the following equations:

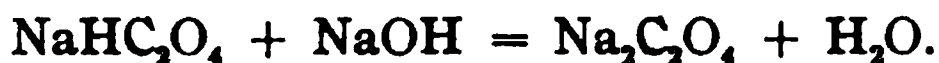
Upon boiling the original solution



and upon titration in the cold



while



3. Effect of Impurities on Standardizing Value.—The errors caused in the use of sodium oxalate by a given amount of such impurities are as follows: When the sodium oxalate is used as an acidimetric standard, Na_2CO_3 causes a positive error to the extent of 21% of its amount, *i. e.*, the material is apparently stronger than 100%. NaHCO_3 causes a negative error of 25% of its amount, while NaHC_2O_4 produces a negative error of 67% of its amount; that is, the same quantity of alkali is present (after ignition) in 134 parts $\text{Na}_2\text{C}_2\text{O}_4$, 106 parts Na_2CO_3 : 168 parts of NaHCO_3 , or 224 parts of NaHC_2O_4 . If sodium oxalate is to be used as an oxidimetric standard, either Na_2CO_3 or NaHCO_3 is an inert impurity, *i. e.*, its effect is proportional to its amount. NaHC_2O_4 causes a positive error of 16% of its amount, since 112 parts of NaHC_2O_4 have the same reducing power as 134 parts of $\text{Na}_2\text{C}_2\text{O}_4$. The same relations may be expressed as follows: In order to have an error in titration of not over 0.10%, the following amounts of impurities may be present: in alkalimetry, 0.48% Na_2CO_3 , 0.40% NaHCO_3 , or 0.15% NaHC_2O_4 ; in oxidimetry 0.10% Na_2CO_3 or NaHCO_3 , or 0.63% NaHC_2O_4 . For use as a general standard, however, the lowest of each of these values is the maximum permissible for the given degree of accuracy.

¹ It is immaterial whether oxalic acid or some stronger acid be employed, since the latter, in small amount, would immediately liberate its equivalent of oxalic acid.

IV. Summary.

1. The solution of pure sodium oxalate is alkaline.
2. Decimolar sodium oxalate solution produces a color with phenolphthalein equivalent to 4% transformation of the indicator, and fifth molar a color equal to 6% transformation. The most probable value of $[H]_{18}$ for such solutions is 2.5×10^{-9} and 2.0×10^{-9} , respectively.
3. The use of calculated standards of (a) phenolphthalein, (b) ammonium chloride and hydroxide, (c) sodium acetate, (d) borax and hydrochloric acid, or (e) glycoll and sodium hydroxide, for determining the normal alkalinity of sodium oxalate is inaccurate, due either to uncertainty in the values of the constants, to undetermined influences of the salts, or the abnormal ionization and hydrolysis phenomena.
4. The value of the ionization constant K for phenolphthalein is probably less than 1.7×10^{-10} for solutions in which it is transformed to the extent of less than 8%, *i. e.*, the only solutions adapted to direct optical comparison.
5. Sodium oxalate solution does not decompose appreciably on boiling.
6. Sodium oxalate solutions readily attack glass, "Durax" glass being the least affected of the kinds tested.
7. Commercial samples of sodium oxalate, dried at 240° , may contain $NaHCO_3$ or even occluded CO_2 .
8. The following method for testing the neutrality of sodium oxalate is recommended to replace that given by Sørensen. Evaporate 200 cc. of water in a quartz or Durax glass flask to 150 cc. in a current of pure air, free from carbon dioxide. Add exactly 0.2 cc. phenolphthalein solution (1% solution in alcohol), and 4 g. of sodium oxalate. Continue to boil for ten minutes, then cool to room temperature while maintaining the air current. If pure, the solution should have a pink color equivalent to 6% phenolphthalein transformation. (Such a standard may be prepared by adding 0.2 cc. phenolphthalein to 150 cc. of water containing 10 cc. of 0.1 N sodium hydroxide, and diluting 9 cc. of this solution to 150 cc.) Each cc. of $N/100$ acid or alkali required to titrate to the standard color indicates the presence respectively of approximately 0.04% $NaHCO_3$ or 0.03% $NaHC_2O_4$. One or two water recrystallizations in platinum will usually be sufficient for the preparation of the pure salt from materials containing a moderate excess of alkali or acid.

The author desires to express his thanks for the information furnished by J. H. Hildebrand, J. Johnston, W. C. Bray and W. F. Hillebrand during the course of this investigation.

FURTHER STUDY OF THE ATOMIC WEIGHT OF MERCURY,
THROUGH THE ANALYSIS OF MERCURIC BROMIDE.

BY C. W. EASLEY AND B. F. BRANN.

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Two previous contributions¹ relative to the atomic weight of mercury described work which resulted, within narrow limits, in the same value of this constant. The methods employed, entirely different in character, dealt with the same material, mercuric chloride. While such a procedure probably indicated that the error of method was sufficiently small to be negligible, doubt pertaining to the nature of the material analyzed was not removed. It remained, then, to prepare material of a different character and it was decided to attempt a redetermination of the atomic weight from a study of the bromide since there seemed to be no reason why this compound should not be prepared in a pure state. It would be ideal to attack the question through the use of the oxide but, from preliminary experiments, the preparation of this compound seems exceedingly doubtful.

The problem with the bromide presented many points of similarity to that of the chloride. Owing to the solubility of silver bromide in mercury salts, instead of treating a solution of mercuric bromide directly with silver nitrate, the mercury was first removed. This was accomplished in two ways, each leading to practically the same results: first, by means of hydrazine hydrate in weak alkaline solution and, second, with hydrogen peroxide under similar conditions. Like results from the use of the two reducing agents would seem to preclude the possibility of any considerable error arising from the use of either. The mean value of the atomic weight found does not differ essentially from the results reported in previous communications.

Pure Mercuric Bromide.

It is well known that bromine may be readily made very pure by the methods of Stas² and the modifications proposed by others³ and, in a previous paper,⁴ several methods for the preparation of pure mercury were described. Thus, since the elements unite easily, it is possible to prepare the bromide of mercury without the intermediate use of water. This is probably important as it was shown in the preparation of the chloride that that salt could not have had contact with water without the production of basic material during the subsequent process of sublimation. There was no reason to expect a different result with the bromide so that recrystallization of the salt was not resorted to, especially when

¹ Easley, *THIS JOURNAL*, 31, 1207 (1909) and 32, 1117 (1910).

² *Oeuvres Complètes*, 1, 587.

³ Richards, *Proc. Amer. Acad.*, 25, 199. Scott, *J. Chem. Soc.*, 77, 649. Baxter, *THIS JOURNAL*, 28, 1322 (1906).

⁴ Easley, *THIS JOURNAL*, 31, 1216 (1909).

the alternative and preferable procedure of bringing pure bromine and pure mercury together in an indifferent medium of nitrogen at the temperature of sublimation was practicable. The bromide thus prepared is probably free from the bromides of other metals for the process was carried out at a temperature in the neighborhood of 300° , conditions under which other compounds, most likely to be present, would not be perceptibly volatil.

In detail, the process consisted in passing a stream of nitrogen through liquid bromine, thus sweeping the vapor into a chamber containing mercury maintained at a temperature of 300° . The apparatus is shown in Fig. 1. The nitrogen was sent through a purifying and drying train constructed of glass alone and the exit tubes were so arranged by means of branches and glass stopcocks that the gas could either first bubble through the bromine in a wash bottle or pass directly into the reaction chamber *C* as shown in Fig. 1. Solutions of potassium hydroxide,

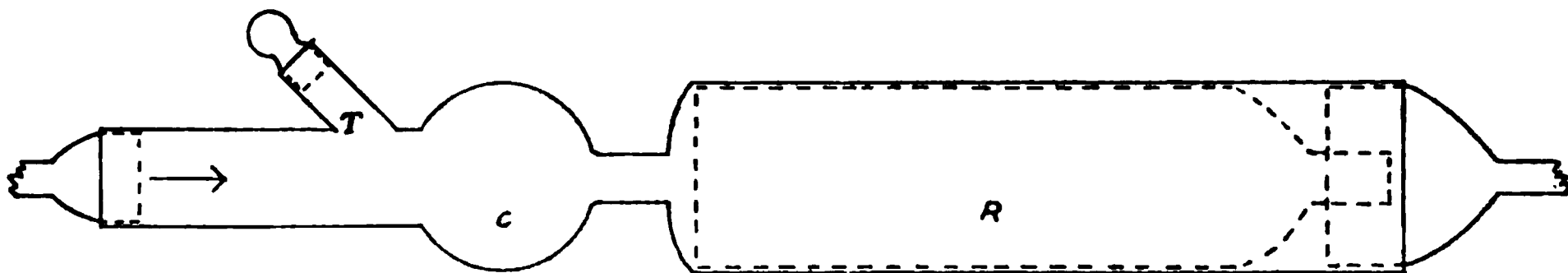


Fig. 1.

some containing lead oxide in solution, were used for purifying the nitrogen while the gas was dried by means of sulfuric acid in towers filled with glass beads. Phosphorus pentoxide, resublimed in a stream of dry air, by contact served to dry the liquid bromine. After pure mercury had been introduced through the tubulature *T* by means of a funnel reaching to the bottom of the chamber *C*, the air in the apparatus was displaced by nitrogen and this in turn by a mixture of nitrogen and bromine. The bulb was then heated to a temperature around 300° . The fact that the metal was covered with transparent, colorless, fused bromide showed that a sufficient excess of bromine was present. When the mercury was entirely converted and carried into the receiver *R* in the adjacent compartment, the latter was raised to a temperature of 235° , a point where the salt began to show a considerable vapor pressure. During the latter operation, nitrogen, without bromine, was passing through the apparatus, completely sweeping out the excess of bromine and liberating, probably, any that might possibly have adhered to the salt at the lower temperature. Air ovens, entirely separate from each other, were used for heating the compartments and these were constructed of asbestos, with glass windows. The temperature was regulated by means of burners below the ovens. After cooling in the same atmosphere, dry air was admitted and the salt was transferred by holding the receiving funnel *R* over the mouth of the

weighing bottle and pushing the crystals into the latter with a well-rounded glass rod. At times, the end of the receiver nearest the chamber C was heated to such an extent by conduction that a portion of the crystals fused and adhered somewhat to the glass. No attempt was made to dislodge such material so that the collected salt must have been entirely free from silica and other matter originating in the glass. The transfer of the salt to the weighing bottle was made in air, for it was shown that exposure to the air of the laboratory did not sensibly affect its weight. In proof, a light tube, sufficiently small to rest on the balance pan, was sealed at one end to another tube of smaller bore through which either dry air or bromine vapor could be admitted. The other end was fitted with a hollow stopper which could be closed by means of a stopcock. A quantity of mercury was converted into the bromide within this tube and as a stream of dry air was passing, it was effectually sealed, at one end by means of the flame and at the other by turning the stopcock. When counterpoised by a similar tube on the balance pan, the stopper was removed and for the first time the salt was exposed to the air of the laboratory.

The salt collected in the receiver in beautiful needle-like masses. The fact that bromine was present in excess during the preparation and that the bromine, mercury, nitrogen and air were free from water would preclude the formation of either calomel or basic salts. The complete solubility of the salt prepared by this method, in fact, shows no impurities of this character.

Preparation of Bromine.

Three samples of bromine were prepared, two being made by well-tried methods in which a solution of calcium bromide was depended upon to react with chlorine and fractional distillation, after transformation to hydrobromic acid, to remove the iodine. The bulk of the mercuric bromide was made with such bromine, but it was decided to use more exhaustive means in the purification of a third sample so that its value could not be doubted. The methods adopted were so laborious that only a small amount of this sample was obtained. The analyses showed that the mean atomic weight does not differ from the mean of any series in which a particular sample of bromine was used, by more than one part in ten thousand.

Sample 1.—Commercial bromine was dissolved in a solution of calcium bromide which was prepared from marble and hydrobromic acid. The marble had not been exposed to the fumes of the laboratory while the acid had been prepared from the original bromine by reduction. The bromine was distilled by placing the solution in a glass-stoppered flask whose side arm was sealed to the condensing system. All save the first fraction of this bromine was covered with sufficient water to form the

constant boiling mixture of hydrobromic acid corresponding to the amount of bromine used. Hydrogen sulfide, from ferrous sulfide and dilute sulfuric acid, was next passed until nearly the whole of the bromine was converted into hydrobromic acid. Hydrochloric acid was removed from the gas by a train of wash bottles, the first of the series being filled with alkaline sulfides and the final ones with pure water. When the sulfur had been separated by filtration through glass wool, the acid was distilled, the free bromine and iodine passing over in the first fraction.

At this stage, the purity of the bromine was investigated. Accordingly, a weighed amount of silver was converted into silver bromide by using some of the hydrobromic acid prepared above after it had been treated with a slight excess of ammonia. The silver was prepared following the ammonium formate method of Stas, with subsequent fusion on lime. Using all precautions, three determinations were made in which 18.32765 grams of silver formed 31.89761 grams of silver bromide. This results in a ratio of 57.457 whereas the theoretical one is 57.445. An excess of chlorine in the bromine is thus indicated. During the next process, however, in converting the acid to bromine, any free chlorine would be in contact with a solution of potassium and manganese bromides and must have been effectually removed.

The oxidation of the acid to bromine was accomplished with potassium permanganate. Kahlbaum's highest grade was found to contain such small amounts of chlorine that several recrystallizations removed all save the merest traces. In fact, tests on the mother liquor of the last crystallization showed a maximum of one part of chlorine in forty thousand parts of salt. The hydrobromic acid dropped from a separatory funnel upon the permanganate in a flask whose connections with the condensing system and funnel were all of glass. The contents of the flask were kept at a temperature such as would liberate the bromine. A first small fraction was discarded. The remainder was freed as much as possible from water by means of a separatory funnel after which it was preserved in a bottle with phosphorus pentoxide, the preparation of which has been described before.

Sample 2.—This sample was prepared in the same manner as Sample 1 save for the fact that sulfur dioxide instead of hydrogen sulfide was used as the reducing agent. The gas was furnished from a cylinder containing the liquid and was allowed to run through several wash bottles containing sodium acid sulfite and then through pure water. This method obviates the contamination of the hydrobromic acid with precipitated sulfur, a source of considerable difficulty combined with loss of material whenever the hydrogen sulfide method was used.

Sample 3.—A quantity of Kahlbaum's best bromine was allowed to remain in contact with a solution of the potassium and manganese bro-

mides which were saved in the process of oxidizing the hydrobromic acid of Samples 1 and 2. The mixture was frequently shaken and finally distilled. Reduction to hydrobromic acid was carried out as in Sample 2 but only the middle fraction of the distillate was retained. To a very dilute solution of this acid, pure silver nitrate was added and the precipitate was washed many times, first with cold and then with hot water. Mercuric nitrate, prepared from mercury and halogen-free nitric acid, was added and allowed to remain in contact with the precipitate for 48 hours. A strong solvent action is thus exerted upon the silver halides¹ and, as the solution of the nitrate was about normal, amounts of chlorine and iodine which analysis revealed in Sample 1 would have been removed when the residue was washed free from the mercuric nitrate. The silver bromide was next suspended in water and converted to hydrobromic acid by well-washed hydrogen sulfide. A reserve supply of the silver bromide used up the excess of hydrogen sulfide. When the sulfide had been separated from the acid, the latter was distilled and oxidized to bromine precisely as in the case of the other samples.

Preparation of Mercury.

Sample 1.—This consisted of a small amount of mercury remaining from previous work.² Its preparation has been described.

Sample 2.—The starting point was the same mercuric chloride whose analysis,³ after sublimation, has already been reported. It was exceedingly pure. After sublimation in a stream of pure, dry air, the salt was dissolved in water and treated directly with an ammoniacal solution of hydrogen peroxide. The resultant globule was given the same treatment as the one to be described under Sample 3.

Sample 3.—The same material used in Sample 2 served as the basis of this sample. The salt was resublimed, dissolved in a large amount of water and treated with sulfur dioxide, thoroughly washed. The precipitated calomel was washed many times with pure water and finally subjected to the action of ammonia. After washing out the excess of ammonia, a necessary process to prevent the formation of large amounts of soluble compounds⁴ from which mercury could not be separated by the method used, sulfur dioxide was again added. During the latter process, the mass was maintained at a temperature of approximately 100°. Metallic mercury separated in globular form. The globule was washed with water and then shaken with a dilute ammoniacal solution of hydrogen peroxide to remove all suspicion of reducible, surface impurities. The metal was dried by quickly heating to the boiling point.

¹ Morse, *Z. physik. Chem.*, 38, 705.

² THIS JOURNAL, 31, 1217 (1909). See sample 3.

³ *Ibid.*, 32, 1125 (1910).

⁴ P. de Saint-Gilles, *Annalen der Chemie*, 84, 266.

Traces of foreign material, of the nature of finely-divided silica, were separated by filtering the metal through a small funnel, the drawn-out stem of which was filled with fine glass threads. In spite of these precautions, after the metal had been converted to the bromide in the apparatus shown in Fig. 1 and the bromide had been distilled, there sometimes remained a slight residue. As no less than 15 grams of mercury was ever used and as the residue seemed unweighable, no error could have crept into the results from this source. No matter how long the residue was heated, no volatilization was apparent. In several cases the residue was certainly silica. At another time, black material remained. This may have been a basic salt of mercury with an inappreciable vapor pressure at the temperature used. How it might have formed is not clear.

Reagents.

Hydrazine Hydrate.—Hydrazine sulfate was treated with an excess of sodium hydroxide and the liberated hydrate was separated by distillation in a copper retort. The product was subjected to a second distillation in a system made entirely of glass. A product almost entirely free from chlorine resulted. When treated with silver nitrate, 0.00003 gram of silver chloride was found in every gram of the hydrate.

Hydrogen Peroxide.—Merck's 30% solution of hydrogen peroxide was redistilled and diluted to an approximately 3% solution. In every 100 cc. used, an amount of chlorine corresponding to 0.00007 gram of silver chloride was found and duly corrected for.

Sodium Hydroxide.—Very pure sodium was converted into the hydroxide by standing on platinum gauze over a platinum dish in a water-laden atmosphere free from carbon dioxide. The required quantity of hydroxide for one determination was prepared at a time and a portion of this material was always examined for chlorine. When treated in the nephelometer¹ with silver nitrate, the different samples showed varying amounts of silver chloride but in no case was an amount present exceeding 0.0001 gram per 5 grams of sodium hydroxide.

Other reagents: The water, nitric acid and ammonia were all redistilled, the first twice from permanganate solution. All were chlorine-free. Silver nitrate was made from the metal and acid and the solution was evaporated to dryness. The metallic silver was prepared by the action of ammonium formate on silver nitrate.

The Method of Analysis.

The plan pursued consisted in treating a weighed amount of mercuric bromide in solution with sodium hydroxide, adding such an amount of a reducing agent as would precipitate the mercury, leaving the bromine in the form of bromide ions. The mercury being filtered off and the solu-

¹ Richards and Wells, *Am. Chem. J.*, 31, 235 (1904).

tion being rendered alkaline, silver nitrate was used to form silver bromide which was weighed. The value of the ratio $\text{HgBr}_2 : 2\text{AgBr}$ is thus determined.

In order to keep the amount of solution at a minimum, the bromide was not entirely dissolved in water when the calculated amount, plus 0.25 or 0.30 gram, of sodium hydroxide was added. The object was not to unduly dilute the reducing agents in which case more mercury might remain in solution and also to avoid the filtration of large quantities of solution. This practice, on the other hand, lengthened the time required for the completion of the reaction since the undissolved crystals of bromide could give rise to an amount of oxide only proportional to their surface. With hydrazine hydrate, the reduction proceeded with relative rapidity at room temperature but in the case of hydrogen peroxide, a temperature of 70° was required to have the reaction progress at a moderate rate. The oxide, successively formed, remained as a crust on the crystals until reacted upon by the reducing agent. Hydrazine hydrate was employed in some of the preliminary work on the analysis of mercuric chloride but no actual analyses were made. It has proven a most effective reagent in the case of the bromide, the mercury forming with perhaps less unglobulized material than in the case of hydrogen peroxide. This, perhaps, is explained by the fact that the reaction is completed more quickly and therefore less silica is formed by the action of the slightly alkaline solution. Again, the temperature was lower. The rate of the reaction was so regulated that the nitrogen was expelled quietly carrying no spray beyond the catch system. A very small amount of mercury must have remained in solution as invariably silver bromide was detected after an excess of silver nitrate had been added. The determination of this dissolved material will be described later. The amount of silver bromide in this condition never exceeded 0.001 gram per liter of solution. When the reduction was complete, the contents of the flask were brought to the boiling point in order to decompose the greater portion of the peroxide. This was done even in the experiments where hydrazine hydrate was used, for the excess of the latter was destroyed by the addition of hydrogen peroxide.

The flask, with the system for introducing the reagents and the tube for the escape of the liberated gases, is shown in Fig. 2. It is of the Erlenmeyer form, holds 500 cc. and is made of Bohemian glass. The tube passing through the ground-glass stopper is branched above. Through one branch the reagents are added and the amount added at any time is gauged by means of the stopcock; through the other, the liberated gases pass. In the latter arm, the tubing is bent so as to form a trap, *T*, beyond which it is widened and filled with beads kept wet with pure water. As the trap is always full of water, a most effective means of

preventing loss through spray is at hand. Any material collecting on the inner walls of the branches found its way into the flask during the rinsing process at the completion of the reduction. It was found very difficult

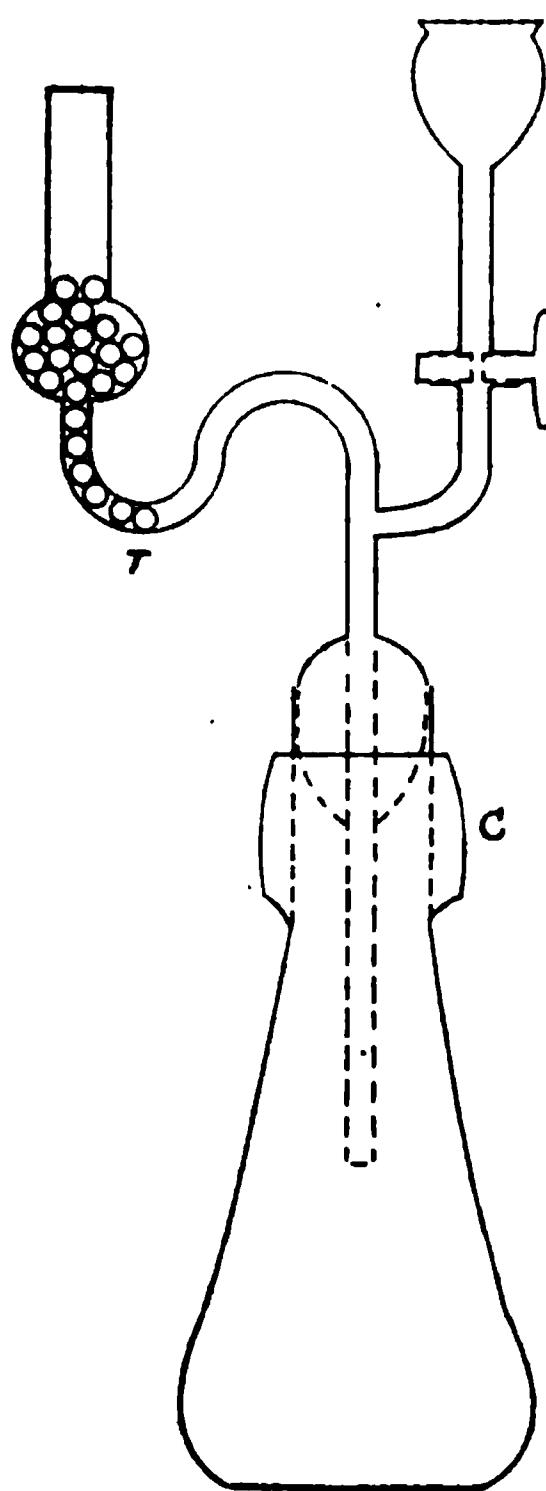


Fig. 2.

in the work on the chloride to entirely separate the mercury from the solution. The extremely fine particles refused to be globulized and some of these particles either passed through the filter paper of the most compact texture or crept over its side. The present work was not unlike the previous case in this respect. Better results were obtained by decreasing the rate of filtration by placing a globule of mercury in the apex of the filter. The difficulty was not entirely overcome, however, so that more than one filtration was often necessary. In spite of the character of the paper used, some shreds were loosened and passed into the filtrate, owing perhaps to the hot, slightly alkaline solution. The amount was very small but it was found later in the fused silver bromide as a small patch of surface scum. It was impossible to determine its amount accurately, but there is little doubt but that the correction would be exceedingly small. All danger of losing any of the solution by leakage from the lip of the flask during filtration was avoided by the use of a protecting cup around the neck of the flask as shown in the figure at C. The cup was thoroughly rinsed after all traces of solution had been removed from the

flask itself. It is safe to say that there was no appreciable loss of material due to the process of filtration. Many rinsings were made, no danger of adding too much water being feared since there is less danger of including material in the precipitated silver bromide if the solution is dilute. The solution was filtered directly into a flask of Jena glass and was acidified with an amount of nitric acid slightly in excess of that found necessary from the known excess of sodium hydroxide used at the outset. A slight excess over the theoretical quantity of silver nitrate was added to precipitate the bromine. Both the bromide and silver solutions were approximately tenth-normal. After standing over night in the glass-stoppered flask, the solution could be easily separated from the precipitate by the use of the Neubauer crucible. Only a small portion of the silver bromide found its way into the crucible during the filtering process, the greater portion remaining in the flask so that the washing might be more effective. The first stage of the latter process consisted in making

eight or ten additions of water containing a slight amount of silver nitrate and nitric acid, decanting each in turn. About the same number of washings were then made with water containing nitric acid alone. The latter washings contained dissolved silver bromide. The amount was determined in the nephelometer and found to average 0.0002 gram per liter. When the precipitate had been completely transferred the crucible with its contents was dried in an air oven, protected from outside fumes, at a temperature ranging from 150–160°, after which it was weighed. The greater portion of the precipitate being transferred to a weighed porcelain crucible and fused, the expelled water was determined by another weighing. The fused mass was transparent, save for a small patch due to filter shreds referred to before, and greenish yellow in color. No difference appeared in the results whether a fused sample contained the above-mentioned impurity or not so that the error from this source is too small to be feared. Since tests on the contaminated portions for silver were negative, it is doubtful if any chemical change had resulted. More likely, the shreds merely entangled and kept separate small portions of silver bromide.

A correction, of small though positive value, became necessary through the observation that bromine was present in the filtrate, after the separation of the silver bromide, even after an excess of silver nitrate was added. This never amounted to more than 0.001 gram of silver bromide per liter, generally considerably less, but a measurable quantity was invariably present. In most cases, the atomic weight would hardly be changed one unit in the second decimal place by this factor but it was determined in every case to guard against larger error. A similar result was found in the analysis of mercuric chloride. At that time, it was assumed to be due to the presence of mercury salts in solution. While no other supposition is put forward here, it is difficult to understand how such small quantities of mercury as are present (none has been shown in tests) could have such a strong solvent action. It is not impossible that some of the finely-divided mercury escaped notice and was dissolved by the very dilute nitric acid added to neutralize the solution. That bromine was present, however, was proven by carrying out a blank test at the same time the solution was examined. The two sets, one with the solution, the other with pure water, were treated alike in every detail and although halogens were always found in the blank due to the reagents, yet larger amounts were always found in the solution. The method of determination consisted in the precipitation of the heavy metals in slightly ammoniacal solution by means of hydrogen sulfide. A small amount of alum in the solution assisted in securing a clear filtrate. Boiling served to drive off most of the hydrogen sulfide and the remainder was oxidized to sulfuric acid by means of hydrogen peroxide. On acidify-

ing the solutions, tests for the presence of halogens were made with the aid of the nephelometer.

As an illustration of the relative value of the corrections necessary in finding the amount of silver bromide which results from a given weight of mercuric bromide, we may take experiment No. 9. In this case, 11.28487 grams of mercuric bromide gave rise to 11.75970 grams of silver bromide, the latter weight being the sum of various factors as follows:

Weight of silver bromide dried at 150–160°.....	11.76077
Weight of silver bromide in filtrate (1225 cc.).....	0.00025
Weight of silver bromide in wash water (1020 cc.).....	0.00020
	<hr/>
	11.76122
Water in silver bromide dried at 150–160° (loss on fusion).....	0.00134
Silver chloride, due to chlorine in hydrazine hydrate.....	0.00002
Silver chloride, due to chlorine in sodium hydroxide.....	0.00016
	<hr/>
	0.00152
	<hr/>
Corrected weight of silver bromide.....	11.75970

The weighings were made by the method of substitution by the use of a delicate Sartorius balance and the weights found in air have been converted to weights in a vacuum by the use of the following corrections:

+ 0.000067 gram per gram of mercuric bromide.

+ 0.000041 gram per gram of silver bromide.

The platinum plated weights were carefully calibrated and the corrections duly applied.

THE RESULTS.

No. of exp.	Sample Hg. Br.		Weight of HgBr ₂ .	Weight of AgBr.	The atomic weight ¹ of Hg.
1.....	1	1	8.93958	9.31480	200.63
2.....	1	1	14.36691	14.96940	200.64
3.....	2	1	10.13638	10.56230	200.61
4.....	2	1	9.94452	10.36218	200.62
5.....	3	1	12.60142	13.13051	200.63
6.....	3	1	12.16157	12.67122	200.65
7.....	3	2	11.19762	11.66809	200.62
8.....	3	3	16.16607	16.84235	200.68
9.....	3	2	11.28487	11.75970	200.59
10.....	3	2	17.25074	17.97597	200.61
11.....	3	3	14.20924	14.80685	200.61

Mean, 200.64

Any discussion of the results would practically be a repetition of that in the paper on the chloride. No evidence has been unearthed in the present work to allow a different view of the result. Hydrogen peroxide

¹ These results are calculated with the values Br 79.92, Ag 107.88; THIS JOURNAL, 33, 1642 (1911).

was used as the reducing agent in eight experiments of the series; in Experiments 9, 10, and 11, hydrazine hydrate served this purpose. The mean result by each method is practically the same. This is strong evidence that there is little error connected with the removal of the mercury from mercuric bromide. The results are slightly but uniformly lower, however, in the cases where hydrazine hydrate was used. This would indicate that all the bromine from mercuric bromide had not been measured when hydrogen peroxide was used or, on the other hand, that foreign matter was weighed in the other series. The latter assumption would seem to be the more probable, if either carries any weight, for hydrazine hydrate, if any remained after the treatment with hydrogen peroxide, might reduce the silver nitrate and thus give an apparently large amount of silver bromide. This seems unlikely, however, for the solution was purposely made more strongly acid in this case than where the peroxide was used in order to counteract such a tendency. The effect is certainly small and should be connected with the accuracy of the second, rather than the first decimal place.

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RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

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The past year has witnessed no startling discoveries in the field of inorganic chemistry, yet there has been great activity along every line, especially in working over old material in the light of new theories. Such work is often difficult and painfully slow, attracts little attention and adds little to reputation, but is vitally necessary if we are to broaden our generalizations. But one new element has been added to the list, Urbain's keltium (Ct) from the gadolinite earths, unless we are to believe the newspaper statements of a new platinum metal from the northwest, and while Ramsay has given radium emanation standing as niton, doubt has been thrown on Flint's companion to tellurium.

No attempt will be made to review the whole field, but rather to consider some of the most important papers which have appeared the past year. The order followed will be that of the periodic table.

Group III.—Further work has appeared from Biltz (*Z. anorg. Chem.*, 71, 182, 427) on the sulfides of this group. Al_2S_3 is prepared by fusing together the metal and sulfur in a crucible and then igniting the mass by magnesium ribbon. The material is then sublimed, best in a vacuum. The felted product consists of fine needles, which are quite possibly isomorphous with corundum, and this is the more probable since the solidifying curve with alumina indicates the formation of mixed crystals ("Mischkrystalle"), though the intersolubility is not unlimited. Al_2S_3 is readily attacked by moisture, and seems to form one or more compounds with the Al_2O_3 formed. The product obtained by Regelsberger from alumina and sulfur in the electric furnace is a complex mixture, but one of its

constituents is the monosulfide, AlS , which is more difficultly volatile than Al_2S_3 . The latter fuses at 1100° . A sulfide of lanthanum is formed by heating the sulfate in a stream of hydrogen sulfide, which gives hydrogen persulfide with acids and has the formula $\text{La}_2\text{S}_3\text{S}$. It loses sulfur above 600° giving La_2S_3 , which shows no sign of fusion or sublimation at 1000 – 1250° in a vacuum, but which is hydrolyzed very actively by water. When praseodymium sulfate is heated in hydrogen sulfide only an oxy-sulfide is formed, Pr_2SO_2 , but if cerium is present, even in minute quantity, as an "inductor," $\text{PrS}_2(\text{Pr}_2\text{S}_3\text{S})$ is formed, and this loses sulfur in a stream of hydrogen sulfide at 600 – 700° , with the formation of the sesquisulfide, Pr_2S_3 . This reaction is delicate enough to detect the presence of cerium in praseodymium compounds, and corresponds to the superoxidation of praseodymium in the presence of cerium.

By the use of his bromate method James (THIS JOURNAL, 33, 1332) has prepared pure thulium and describes a number of its salts. All attempts to resolve it by fractional crystallization failed, no change in its absorption spectrum appearing after about 15,000 operations.

In the *Journal of Industrial and Engineering Chemistry*, (3, 299), Weintraub describes the preparation and properties of pure boron. It may be prepared by the action of magnesium on the oxide; the suboxide, B_2O , as well as other impurities are removed by heating to 2000° , at which temperature they dissociate. A second method of preparation is by heating BCl_3 (from the action of chlorine on the carbide) with hydrogen. Pure boron is black, amorphous, and exceedingly hard, only being surpassed by the diamond. It shows traces of volatilization at 1200° but fuses only above 2000° . Its most remarkable property is the increase of its electrical conductivity with the temperature. In the cold it is a poor conductor, its specific resistance being 10^{12} times that of copper. At 400° its specific resistance has decreased in the proportion $2 \times 10^6 : 1$. Weintraub suggests that this property may give it important industrial applications.

Group IV.—A very suggestive attempt to study the association of silicate minerals from the standpoint of heterogeneous equilibrium is made by Sosman (*J. Wash. Acad. Sci.*, 1, 54), who treats the mixture of the metasilicates of Mg, Ca, and Fe as a three-component system, plotting the analyses of the various minerals and rocks made up of these constituents (by triangular coordinates). He finds a boundary line between the mineral analyses and rock analyses, which he considers to represent the boundary between magma compositions that will form homogeneous solid solutions and those that will separate into two different solid solutions between which is a eutectic. The rock analyses lie in the "eutectic field," the minerals outside of it. The two types of minerals of which these rocks are made up are in each case the two solid solutions which appear on opposite sides of the "eutectic field." A much broader generalization is attempted by Goldschmidt (*Z. anorg. Chem.*, 71, 313) who treats mineral association from the standpoint of the phase rule. He uses the following form of the rule "the maximum number n of solid minerals which can exist together in stable form is equal to the number n of components which the minerals contain." This is true for any arbitrary temperature and any arbitrary pressure. At a definite "singular" temperature (transition-temperature), or pressure, $n + 1$ minerals can coexist. He discusses numerous illustrations, SiO_2 , as a one-component

system, $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, as a two-component system, $\text{CaO}\cdot\text{TiO}_2\cdot\text{SiO}_2$, as one of three components, and cites instances of the practical value of study from this standpoint. Last year Cambi described a monosulfide of silicon formed by the action of sulfur on ferro-silicon in the electric furnace. This existed in two forms, one black and compact, and the other a yellow powder, formed from it by sublimation. He now presents (*Atti accad. Lincei, Rome*, [5] 20, i, 433) a more extended study of these compounds. The yellow sulfide is acted on violently by water with the evolution of hydrogen, but by care the white hydrolytic product can be obtained without decomposition and proves to be the anhydride of silico-formic acid, $(\text{HSiO})_2\text{O}$. This has strong reducing powers and at 400° decomposes into hydrogen and SiO_2 (with some free Si). The $\text{Si}(\text{OH})_2$, evidently first formed on the hydrolysis of SiS , passes by tautomeric change into silico-formic acid, analogous to the tautomerism of $\text{Ge}(\text{OH})_2 \rightleftharpoons \text{HGeO}\cdot\text{OH}$ described by Hantzsch. By the action of dry HCl on the yellow SiS , silico-chloroform is formed: $\text{SiS} + 3\text{HCl} = \text{H}_2\text{S} + \text{SiHCl}_3$. The hydrolysis of the black silicon monosulfide is very different from that of the yellow, giving among other products SiO_2 , and Cambi concludes that it is the product of a decomposition of the yellow sulfide, $2\text{SiS} = \text{Si} + \text{SiS}_2$, the transition temperature being slightly below 1000° , the sublimation point of SiS , and above which temperature only it is the stable form. In this connection note may be made that Besson and Fournier (*Compt. rend.*, 151, 1055) have found that the product when dry HBr is led over amorphous silicon at a red heat is chiefly SiBr_4 , but that SiHBr_3 is also formed, with a trace of SiH_2Br_2 and possibly SiH_3Br . By the action of the silent discharge silico-bromoform is converted into silico-methane homologues, Si_2Br_6 , Si_3Br_8 , and $\text{Si}_4\text{Br}_{10}$ having been isolated.

Attention is called by Werner von Bolton (*Z. Elektrochem.*, 17, 816) to an interesting biological action of metallic thorium. It was noticed that in distilled water, in which metallic thorium (prepared by the action of Na on ThCl_4) was kept, bacterial-like growths appeared, which was not the case in the presence of other metals. In further experimentation the amphioxus was kept in North Sea water to which metallic thorium and thorium oxide had been added. The animals remained alive much longer than in the absence of thorium, and the preservative action seemed to be proportional to the amount of thorium present and to depend but slightly on the oxide. On the other hand the metal appeared to be injurious to vegetable life, so that possibilities are suggested of destroying bacterial growths on animal life by thorium.

Group V.—In his Baker lecture before the Royal Society, Strutt (*Proc. Roy. Soc. London*, [A], 85, 219) describes a chemically active modification of nitrogen, formed when pure nitrogen is submitted to the electric spark. This modification is characterized by a luminescence which persists for a short time after the discharge has ceased. The luminescence is decreased by heat and increased by cold. This form of nitrogen attacks many elements, forming an explosive compound with mercury. It unites with yellow phosphorus, much red phosphorus being formed at the same time. With iodine a beautiful light blue flame appears, which gives a spectrum with broad bands. With nitric oxide the dioxide is formed, and with acetylene and with organic halides cyanogen is formed, which was recognizable by its spectrum and also by chemical tests. Whether this modification is to be looked upon as atomic nitrogen or as a molecule

of the ozone type does not yet appear. The constitution of the nitroso compounds of ferrous iron and of copper has been further studied by Kohnschütter (*Ber.*, **44**, 1423) and the conclusion reached that the brown color which appears when nitric oxide is led into ferrous solutions is due to the direct addition of NO to the ferrous ion. This is confirmed by the electrolytic migration of the color toward the cathode. The reaction $\text{Fe}^{++} + \text{NO} \rightleftharpoons \text{Fe}(\text{NO})^{++}$ is reversible and the NO absorbed never reaches the proportion of one molecule to each ferrous atom. The capacity of ferrous solutions for nitric oxide increases markedly in the presence of strong acids and here the color changes. In this case the color migrates toward the anode and indicates the formation of a complex anion containing both iron and NO. These complex anions are somewhat more stable than the nitroso-ferrous cations. Blue cupric solutions do not absorb nitric oxide, but those which are green or brown, such as solutions of cupric chloride or bromide in alcohol, acetone, or concentrated solutions in water, form with NO complex anions similar to those with iron. Nitroso-cupric cations are unknown. The author holds that there is no relation between these nitroso compounds and nitroso-sulfuric acid, $\text{H}_2\text{SO}_5\text{N}$, which has been suggested by some chemists.

The composition of solid hydrogen arsenide has been investigated by Reckleben and Scheiber (*Z. anorg. Chem.*, **70**, 255, 275), by determining the amount of arsenic acid and reduced silver after the action of ammoniacal solution of silver on the arsenide and the metallic arsenic which invariably accompanies it. In using this method it is not necessary to isolate the arsenide, hence all risk of oxidation is avoided. The conclusion is drawn that the formula H_2As_2 best satisfies the results obtained. They also find that when arsenic is sublimed in hydrogen no solid arsenide is formed and no considerable quantity of arsine, H_3As , a result to be expected, but not in accordance with the statements of Retgers. They also find that no solid arsenide is present in the black spot produced by cooling the arsine flame, even when an excess of hydrogen is present. It appears that the yellow modification of arsenic has often been mistaken for the solid arsenide. Incidentally the authors note that arsine does *not* have the garlic odor commonly attributed to it, but that this odor is due to the suboxide. An investigation of stibine shows no evidence of the existence of any solid antimonide of hydrogen.

Reference should be made to the exhaustive work of Ruff (*Ber.*, **44**, 506, 2534, 2539) on the halides of vanadium, in which the methods of preparation and the properties of the chlorides, bromides and fluorides are studied, but the articles do not admit of a brief abstract. The solubility of hydrogen in tantalum has been studied by Sieverts and Bergner (*Ibid.*, p. 2394) and it is found that while at 500° the gas-free metal is inactive toward hydrogen, if it has been saturated at higher temperatures it continues to absorb when the temperature is lowered. For a given temperature the solubility is proportional to the square-root of the pressure, and not directly to the pressure, as would be the case if the solubility followed Henry's law. The absorption is endothermic and decreases with the temperature. In most of these respects palladium is the only metal which resembles tantalum, and the solubility of hydrogen in tantalum is of much the same magnitude as its solubility in palladium. In both cases the solubility is due to some combination of the metal with hydrogen, the nature of which is unknown. After absorption of hydrogen, tantalum

wire becomes brittle. The hydrogen can be removed by heating to a red heat in a vacuum, but the wire remains brittle. The reaction between the metal and hydrogen is thus reversible, but the structure change of the metal is not. The original properties of the metal are slowly restored by heating to a high white heat.

Group VI.—The suggestion is made by Ebler and Krause (*Z. anorg. Chem.*, 71, 150) that the name *peroxydate* ("peroxydat") should be used for derivatives of hydrogen peroxide, in order to avoid confusion with peroxides in which the metal has a higher valence; that is, in tautomeric

compounds, $M \begin{array}{c} \diagup O \\ || \\ \diagdown O \end{array} \rightleftharpoons M \begin{array}{c} O \\ // \\ O \end{array}$ or $M = O = O \rightleftharpoons M \begin{array}{c} O \\ // \\ O \end{array}$, the former would be

a peroxydate and the latter a peroxide. It would seem to the reviewer better to confine the term peroxide to the former and to denominate the latter simply as a dioxide. The term peroxide would then be used only for those compounds which on treatment with acids give the reaction for hydrogen peroxide, from which they may be considered as derived. Ebler gives two general methods for the preparation of peroxides, one by the action of metal alkyls on hydrogen peroxide in dry ether solution, and the other the action of metal amides on the same solution. By these methods all secondary hydrolytic reactions are avoided. In this way Ebler has prepared zinc peroxide, which has the formula $ZnO_2 \cdot \frac{1}{2}H_2O$. This is a fairly stable compound which is very slowly hydrolyzed in cold water, and with acids gives the reactions for H_2O_2 .

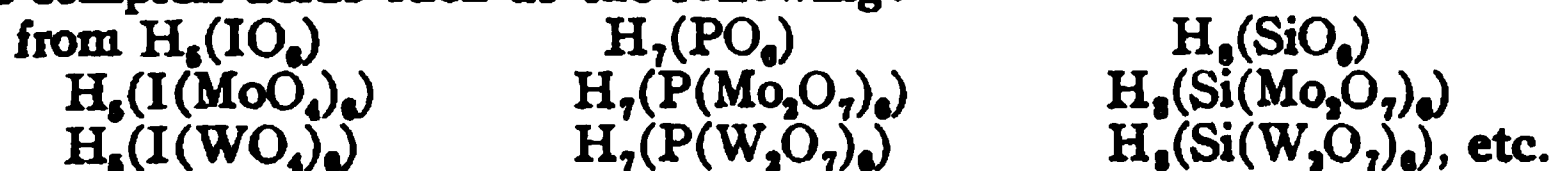
The reaction between SO_2 and NH_3 , to which already so much attention has been given by Divers, Ogawa, and others, has been further studied by Ephraim (*Ber.*, 44, 379, 386, 395), who finds three distinct products: by excess of SO_2 , aminosulfinic acid, $NH_2 \cdot SO_2H$, is formed; by excess of NH_3 , either white ammonium aminosulfite, $NH_2 \cdot SO_2NH_4$, or a red compound with the formula $2SO_2 \cdot 4NH_3$. Since three of the nitrogen atoms differ from the fourth and since a silver salt with three atoms of silver can be formed from it, the red compound must be the tri-ammonium salt of imino-disulfinic acid, $NH_4 \cdot N(SO_2NH_4)_2$. This compound is also formed by the reaction between thionyl chloride and liquid ammonia. By the action of thionyl chloride and hydrazine, an analogous compound is formed, hydrazine-disulfinic acid, $HO_2S \cdot NH \cdot NH \cdot SO_2H$, in which all the hydrogen is replaceable, as by Ba. In the reaction between thionyl chloride and hydrazine a portion of the thionyl chloride is reduced to sulfur which dissolves in the hydrazine with the formation of sulfohydrazinium, which is analogous to sulfammonium, for which Ruff has found the formulas $(S(NH_2)_6)_2$ and $(S(NH_2)_8)_2$ (*Z. anorg. Chem.*, 70, 49). In this connection Ephraim also prepared sulfohydrazide, $SO_2(NH \cdot NH_2)_2$, and nitrosulfamide, $NH_2 \cdot SO_2 \cdot NH \cdot NO_2$, the first representatives of hydrazides of inorganic acids and of inorganic nitramides. In this connection may be noted the first of a series of compounds in which sulfaminic acid takes the place of ammonia in the metal-ammines. By the action of sulfaminic acid on potassium chloroplatinite Kirmreuther (*Ber.*, 44, 3115) has formed two salts of the formula $(Cl_2Pt(NH_2 \cdot SO_2)_2)K_2$, one being a dihydrate but not converted into the other by loss of water of crystallization. These two salts prove to be stereoisomers, the hydrated salt being the *cis*-form. Both salts are neutral but the *trans*-form is converted by caustic potash into a tetra-potassium salt, which

apparently has the formula $(\text{Cl}_2\text{Pt}(\text{NH}.\text{SO}_3\text{K})_2)_2\text{K}_2$, a derivative of an isomeric di-potassium salt, $(\text{Cl}_2\text{Pt}(\text{NH}.\text{SO}_3\text{H})_2)_2\text{K}_2$, which has not been prepared. In discussing the formula of the lead chamber crystals, Jurish (*Chem. Ztg.*, 34, 1065) holds that it is neither a nitro- or a nitrosyl-sulfuric acid, but that the formula must be doubled, as indeed Weber, from whom the acid is often named, suggested. The formula $\text{SO}_2(\text{OH})_2$, which is ordinarily given for sulfuric acid, should be discarded since the acid contains neither SO_2 nor hydroxyl groups, but is rather a compound, after Werner, of SO_3 with H_2O . In the union of SO_3 with H_2O in the lead chamber, when insufficient water is present, instead of forming (double formula) $\text{H}_2\text{O}.\text{SO}_3.\text{SO}_3.\text{H}_2\text{O}$, one H_2O is replaced by N_2O_3 , giving $\text{H}_2\text{O}.\text{SO}_3.\text{SO}_3.\text{N}_2\text{O}_3$, which is the formula of the chamber crystals.

Harcourt and Brereton Baker (*J. Chem. Soc.*, 99, 1311) have repeated the work of Flint on the fractional hydrolysis of tellurium tetrachloride but, contrary to Flint, find no evidence of a fraction with a lower atomic weight for tellurium. They suggest that Flint's results might have been occasioned by the presence of the trioxide. In the course of his extensive work on salts of the type $\text{M}^{\text{II}}, \text{M}^{\text{IV}}\text{Hal}_6$, Gutbier has described (*J. prakt. Chem.*, [2] 83, 145) a large number of chloro- and bromo-tellurates of organic bases, and these have also been crystallographically examined by Lenk. These salts, while soluble without decomposition in very little water, even if warmed, are rapidly hydrolyzed by the slightest excess, and cannot be recrystallized from pure water. They are, however, readily recrystallized from dilute HCl or HBr . In acid solution they act toward reagents in every respect like solutions of TeO_2 in the acid. By passing an electric arc between tellurium electrodes under strongly cooled CS_2 , Stock (*Ber.*, 44, 1832) has obtained carbon ditelluride, CTe_2 , in dilute solution. The compound could not be isolated, but its analysis was determined by its decomposition products. It is exceedingly unstable; its solution is golden-yellow, and when its concentrated solution is cooled to -100° it deposits minute brown crystals. Even in a 0.1% solution its odor is intolerably suffocating. It resembles in many respects the little known CSe_2 .

The "complex" acids containing molybdic, tungstic, and other acids have long interested chemists and many unsuccessful efforts have been made to account for these compounds on valence theories. The application of Werner's theories proved no less elusive until Miolati suggested the resemblance of these acids to salts of the familiar type, $(\text{M}^n\text{X}')^{n-6}$, (such as PtCl_6), where the valence of the ion depends upon the valence of the central atom, being the difference between the valence of this atom and that of the atoms or groups which surround it. We would thus have the ions $(\text{TeO}_6)^{\text{VI}}$, $(\text{IO}_6)^{\text{V}}$, $(\text{PtO}_6)^{\text{VIII}}$, etc. The difficulty of applying this to the complex acids is the same as presents itself in applying it to many of these simpler acids, that frequently the end-form is not developed. Thus in the telluric and periodic acids, the commoner salts are derived from H_2TeO_4 and HIO_4 . Salts of the normal acids, as Ag_6TeO_6 have, however, been prepared. Again, in platinic acid six of the hydrogen atoms migrate within the nucleus and its salts are those of the acid $(\text{Pt}(\text{OH})_6)^{\text{II}}$. The beginnings of Miolati have been followed up in the work of Rosenheim (*Z. anorg. Chem.*, 69, 247, 261; 70, 73, 248; *Z. Elektrochem.*, 17, 694), and he has been remarkably successful in preparing salts of the end-forms of the different types, thus substantiating

the predictions of the theory. In the application of this theory to the complex acids, in the types noted above the oxygen is replaced by bivalent groups, such as MoO_4 and WO_4 , or Mo_2O_7 and W_2O_7 , and we would have as complex acids such as the following:



Now while many of these acids are evidently tribasic, as the familiar phosphomolybdic acid, Miolati had already found by physico-chemical methods that the free acid gave evidence of a higher basicity, and Rosenheim has now prepared the guanidinium salts of phosphomolybdic and of arsenomolybdic acids, in which the acids are actually septi-basic, and yet the salts by conductivity determinations prove to be neutral salts, a remarkable confirmation of theory. In the oxalo-tellurates, telluric acid, of formula H_6TeO_6 (not TeO_3), is actually present in the anion. Meta-

tungstic acid he finds to be an aquo-acid with formula $\text{H}_2(\text{WO}(\text{WO}_4)_3(\text{H}_2\text{O})_3) + \text{aq.}$, and this is confirmed by the fact that the silver, thallium and guanidinium salts all contain three molecules of water. It may, however, be noted that this is contrary to the views of Copaux regarding the water (*Ibid.*, 70, 297). For those "complexes" made up of the same acid anhydrides, Rosenheim proposes the name *isopolyacids*, as polymolybdic acid, while for those which contain different anhydrides *heteropolyacids* is used, as for phosphomolybdic or arsenotungstic acids. This beginning of the systematization of the complex acids will be welcomed by all who have worked on these interesting but perplexing compounds.

Group VII.—The method of preparation of anhydrous chlorides recently developed by Bourion, heating the oxide in chlorine and the chloride of sulfur, has been extended in various directions. Chauvenet (*Compt. rend.*, 152, 87, 1250) finds that by heating in a current of COCl_2 many different oxides are converted into chlorides. The temperatures necessary to induce the reaction vary from 350° for Fe_2O_3 to 650° for ThO_2 . WO_3 forms at 350° the oxychloride WO_2Cl_2 , but in all other cases the chloride was formed. Carbonyl chloride reacts also similarly with sulfides, carbonyl sulfide being the by-product. This reaction is capable of many applications, as in the decomposition of sulfide ores, and their analysis, and also in the preparation of carbonyl sulfide. Michael and Murphy (*Am. Chem. J.*, 44, 365) have studied the reaction between chlorine in carbon tetrachloride solution on many oxides, especially with a view to the positions of the metals in the periodic system, as well as to the relation of unsaturated oxides to chlorine. Thus in the case of FeO , MnO , NiO and CoO , the general reaction is $3\text{MO} + \text{Cl}_2 = \text{M}_2\text{O}_3 + \text{MCl}_2$. With FeO the reaction takes place actively at -18° , while that with MnO is not quite as active. NiO reacts at ordinary temperature, but the reaction is completed only after some time, while with CoO heating in a closed tube to 100° is necessary for the completion of the reaction. In some cases oxychlorides are formed at lower temperatures and chlorides when more highly heated. The action of the $\text{Cl}-\text{CCl}_4$ solution on MoO_3 , and WO_3 would appear to be the best method of preparing MoCl_5 , WOCl_4 , and WCl_6 . In some cases, as with Ag_2O and CrO_3 , the solvent takes part in the reaction, the CCl_4 being oxidized to COCl_2 . The authors call attention to the fact that since chlorine is soluble in CCl_4 to the extent of

10% of its weight at ordinary temperature and 25% at 0°, this solution affords a convenient means of using chlorine in a fairly concentrated condition. Darzens (*Compt. rend.*, 153, 270) has studied the action of thionyl chloride on oxides, and finds that in general its action is similar to that of the $\text{Cl-S}_2\text{Cl}_2$ mixture. In some cases, however, as with WO_3 and with gadolinium oxide, it was found impossible to complete the chlorination, the oxychloride being formed, even at high temperatures and with excess of the reagent. Thionyl chloride offers in no case any advantage over the $\text{Cl-S}_2\text{Cl}_2$ mixture for converting oxides into chlorides, while it is much more difficult to prepare and especially to obtain free from phosphorus. The action of POCl_3 on metallic oxides is the subject of a paper by Bassett and Taylor (*J. Chem. Soc.*, 99, 1402). In some cases, as with the oxides of cadmium, cobalt, copper, mercury, iron and aluminum, the anhydrous chloride of the metal was at least the chief product. In other cases what appear to be addition products were formed, such as $\text{CaO} \cdot 2\text{POCl}_3$ at 110° and $\text{CaO} \cdot 3\text{POCl}_3$ at ordinary temperature, and analogous compounds with MgO , MnO , and ZnO . The fact that these compounds give up their POCl_3 content to petroleum ether would seem to relegate them to the class of addition products, still it is possible that they may be looked on as phosphates in which hydroxyl groups are replaced by chlorine, and their constitution may have a bearing on that of apatite and wagnerite. When the reaction between phosphoryl chloride and oxides was carried out in a solution of acetone or of esters, the solvent took part in the reaction and complex compounds were formed containing the solvent, $\text{P}_2\text{O}_5\text{Cl}_4$, and the metallic oxide. An interesting case of isomerism is noted by Costachescu (*Ann. Scient. Univ. Jassy*, 7, 5) in his study of metallic fluorides. When freshly prepared cobalt hydroxide is dissolved in HF and evaporated in vacuum over H_2SO_4 , large garnet-red crystals are obtained of the formula $\text{CoF}_2(\text{H}_2\text{O})_4$, while, if the original solution is precipitated by alcohol, small rose crystals of the same composition are obtained, but which lose much more water at 60° and which unite directly with pyridine in the cold, while the dark red modification reacts only when heated on the water bath. The isomerism seems to be attributable to the fluorine in the first more stable form being on opposite angles of an octahedron, while in the latter, less stable form, they are on neighboring angles. Both give the same pyridine compound, $((\text{H}_2\text{O})_2\text{CoPyr}_4) \cdot \text{F}_2 + \text{H}_2\text{O}$. With nickel the modification corresponding to the less stable form only was obtained, and this forms with pyridine a compound analogous to that with cobalt. Attention should be called to a paper by Herrmann (*Z. anorg. Chem.*, 71, 257) from the Göttingen physico-chemical laboratory, which opens up a little worked field. It is entitled "The Combining Power of the Chlorides of Copper, Lead, Iron, Tin and Bismuth, and of the Chlorides, Bromides and Iodides of Copper and Cadmium," and is a study of these compounds from a similar standpoint to that of metallography. Where not prevented by the "alloy" being too hygroscopic, microscopic studies were also made. In some cases compounds were found and two eutectics; in others only a single eutectic; in some cases mixed crystals with complete or with limited solid solubility. The paper does not admit of abstraction here, especially as it is quite fully treated in *Chemical Abstracts*, 5, 3545, but it may be noted that no parallel is found between the combining power of metals and of their salts. Further developments along this line cannot fail to

bring out much of interest. Bleaching-powder has been again the subject of investigation, this time by Taylor (*J. Chem. Soc.*, 97, 2541), who finds that when CO_2 is led over bleaching-powder only chlorine is evolved and no hypochlorous acid. The same is true when CO_2 is led into a solution of NaCl and NaOCl . Thus CO_2 acts in this respect like other acids. That HCl is set free by CO_2 may be made evident by leading CO_2 into a solution of NaCl or CaCl_2 containing methyl orange, when the indicator is turned red. If air free from CO_2 is led into a bleaching-powder solution, the evolved gas, which is given off very slowly in the cold but more rapidly when warmed, is almost exclusively HOCl , but with ordinary air which has not been freed from CO_2 , the HOCl is accompanied by chlorine. It is suggested in explanation of these reactions that in bleaching-powder there exists the equilibrium:



The action of CO_2 would then consist in neutralizing the $\text{Ca}(\text{OH})_2$, and thus displacing the equilibrium to the left. Similarly, in bleaching as the chlorine is used up, more is freed and the reaction goes on to the left to completion. This equation would explain why the action of bleaching-powder is more intense in the presence of CaCl_2 in excess, increasing its concentration, and why electrolytic bleach is more active than a mere solution of hypochlorite.

What seems to be a salt of quadrivalent manganese with an oxy-acid has been prepared by Marino (*Atti accad. Lincei, Rome*, [5], 20, i, 447). Analogous with the action of SO_2 , when MnO_2 is treated with SeO_2 , a compound is formed which has the formula MnSe_2O_6 . This is a yellow crystalline powder, insoluble in water and in dilute HNO_3 and H_2SO_4 , but it possesses none of the properties which would be expected of an analog of a dithionate. In concentrated HCl it dissolves with evolution of chlorine, and liberates iodine from an acetic acid-KI solution. With alkali hydroxides and carbonates, MnO_2 is formed, and oxalic acid is oxidized to CO_2 . Numerous other reactions show that it is an oxidizing agent of considerable strength. It thus seems quite certain that quadrivalent manganese is present. Selenous acid is recovered by the action of alkalies, so that the salt is to be looked on as a selenite of quadrivalent manganese, $\text{Mn}(\text{SeO}_3)_2$. By heat it is converted by loss of SeO_2 into manganese selenate, MnSeO_4 , which on further heating is decomposed into SeO_2 and Mn_2O_4 (and O).

Group VIII.—Two papers have appeared on the relation of FeO and Fe_3O_4 to water at moderately high temperatures, the one by Friend, Hull and Brown (*J. Chem. Soc.*, 99, 969), who have studied the action of water vapor on iron, and the other by Hilpert and Beyer (*Ber.*, 44, 1608), who use the reaction between hydrogen saturated with water vapor on ferric oxide. According to the former, the velocity of the reaction between Fe and H_2O , as measured by the increase in weight of the iron, is at 500° practically zero. At 820° and at higher temperatures the iron is completely oxidized to Fe_3O_4 . Between these temperatures the curve of oxygen absorption finally becomes parallel to the time axis, which according to the authors is explicable if it is assumed that at lower temperatures (350°) the dissociation pressure of water is but little greater than that of FeO , but less than that of Fe_3O_4 . Only at 820° does the dissociation pressure of water reach that of Fe_3O_4 . Then we can con-

ceive that at the lower temperature FeO is first formed, and from there to 820° a mixture of FeO and Fe_3O_4 , the dissociation pressure of the oxides being in equilibrium with that of water for each particular temperature. At 820° , the dissociation pressure of water reaching that of Fe_3O_4 , this oxide only will be formed. The authors were unable to bring any direct proof of this view, since they could not reduce Fe_3O_4 in a current of steam. Starting out from the fact that it is impossible to obtain the lower oxides of iron by reduction of Fe_2O_3 in hydrogen or CO, since owing to the removal of the oxidation products the partial pressure of the oxygen remains at zero and hence less than that of the oxide, Hilpert and Beyer inhibit this reduction of the oxygen pressure by carrying on the reduction by a mixture of hydrogen and water vapor. At a red heat the dissociation pressure of the oxygen of water is certainly greater than that of Fe_3O_4 , since the latter is formed by heating the metal in steam. Thus by mixing hydrogen and steam the dissociation of the latter is inhibited to any desired degree, and hence one can prepare mixtures of these gases in which the partial pressure of the oxygen shall correspond to any desired value, between that of the metal and Fe_3O_4 . Experimentally the authors prepared their mixtures by leading hydrogen through water at fixed temperatures; their oxide was pure Fe_2O_3 , prepared from the oxalate, and heating and cooling was carried on in a stream of nitrogen. The composition of the resulting products was determined by loss of weight, and by titration of the ferrous iron and of the total iron. Some 150 experiments were carried out from 300 – 1100° . Between 300° and 400° by using less than 4% of water vapor, all possible stages of reduction of the metal were obtained. When the amount of water vapor passed this limit pure Fe_3O_4 was obtained. In no case was FeO obtained as a definite phase. It is thus possible to prepare pure Fe_3O_4 by heating ferric oxide to 400° in a stream of hydrogen which has been passed through a wash bottle of water heated to 30 – 50° . At 500° a mixed oxide with 50% FeO was obtained, and by using higher temperatures the mixed oxides contained larger proportions of FeO. At 700° the limit is 85% FeO, the limiting proportion of water in the vapor being 38%. Even at 1100° the oxide still contained a minimum of 1.5% Fe_3O_4 , nor does it appear possible by reduction to obtain pure FeO. By starting with pure iron instead of ferric oxide the iron was but slowly attacked by the hydrogen-water vapor mixture, and oxides of indeterminate composition were formed, nor was it found possible by pure water vapor to convert the iron completely into Fe_3O_4 , even after many hours. The magnetic character of the resultant oxides was also examined. This diminishes with increasing amounts of FeO and when between 80 and 90% FeO is present the magnetic quality has well nigh disappeared. Since Fe_3O_4 is paramagnetic it appears that the marked magnetic quality of Fe_3O_4 is due to a compound of the two oxides. The conditions necessary for the formation of iron pyrites are very fully discussed by Feld (*Z. angew. Chem.*, 24, 97, 290), the working of a method for the purification of illuminating gas from H_2S and NH_3 by means of certain iron compounds having led to the discovery of the ready formation of FeS_2 in aqueous solution. If a solution containing iron thiosulfate and iron polythionates is boiled with FeS and sulfur, FeS_2 is formed. It is also rapidly formed when FeS is heated in neutral or weakly acid solutions with excess of sulfur or substances which can readily part with the sulfur which they contain. The presence of basic substances even as weakly

basic as magnesia, hinders the formation of FeS_2 , while the presence of reducing substances promotes the union of FeS and S to FeS_2 . The author suggests that precipitated iron sulfide is actually Fe(OH)(SH) , and that this unites with sulfur, water being split off and FeS_2 formed. Bases or oxidizing substances would antagonize the precipitation of the Fe(OH)(SH) . The following proposition, a modification of that of Bischoff (*Lehrbuch d. chem. u. physik. Geologie*, 1, 917), is laid down: Wherever iron-carrying waters come into contact with reducing substances which can give up sulfur and are not basic, and wherever rocks which contain iron and are not basic come into contact with waters which contain reducing substances and substances which can give up sulfur, there FeS_2 will be formed. This then is the condition of pyrites formation in nature. Rosenberg has concluded his investigations of the nitroprussides by a long paper (*Arkiv. Kem. Min. Geol.*, 4, Nr. 3, 1), in which he considers the mother substance of the nitroprussides to be nitroso-iron trisulfide, $(\text{NO})_2\text{FeS}_3$. This is prepared by leading nitric oxide into a solution of ferrous chloride at -2° and then partially precipitating by the addition of a very dilute solution of sodium trisulfide, though other alkali sulfides will answer. The precipitate is filtered off and nitric oxide and the sulfide again added until the iron has been completely precipitated. Rosenberg considers that a nitrosochloride, $(\text{NO})_2\text{FeCl}_2$, is at first formed, but in view of the fact that ferrous iron will unite with only one nitroso group this may be doubted. The nitroso-iron trisulfide is very stable towards acids but is attacked by alkalies. In sodium sulfide it dissolves with the separation of sulfur and the formation of the red, unstable, nitroprusside. The reaction is: $2(\text{NO})_2\text{FeS}_3 + \text{Na}_2\text{S} = (\text{NO})_4\text{Fe}_2\text{S}_2\text{Na}_2 + 5\text{S}$. By the action of dilute acids, even carbonic, or better by the action of the nitroso-iron trisulfide, the red salt goes over into the stable black nitroprusside: $2(\text{NO})_4\text{Fe}_2\text{S}_2\text{Na}_2 + 2\text{H}^+ = (\text{NO})_7\text{Fe}_2\text{S}_3\text{Na} + 2\text{Na}^+ + \text{NaS} + \text{H}_2 + \text{NO}$. Both salts contain the sexivalent (Fe_2) group, the constitution of the black salt being $(\text{NO})_7\text{Fe}_2(\text{SFe(NO)})_2\text{SNa}$. This indicates why the black salt should be formed by the action of the nitroso-iron sulfide on the red salt. By the action of alkalies the black salt is changed into the red.

The recent work of Werner (*Ber.*, 44, 873, 1887, 2445, 3132) on isomerism in cobalt and chromium bases is hardly surpassed in brilliancy by the classic work on the asymmetrical carbon atom. From the standpoint of Werner's valence theory numerous isomers should be possible among the metallo-bases, though none were known when he suggested his theory. By persistent work these gaps have gradually been filled, giving thereby the strongest substantiation to his theory. In the simple cobalt bases the six atoms or groups surrounding the cobalt atom in the coördinated group are conceived of as situated at the six corners of an octahedron. This group has best lent itself to detection of isomerism when four of the corners are occupied by two molecules of ethylenediamine. In the group X_2CoEn_2 (En is used as the symbol of ethylenediamine) the two groups X may be on contiguous or on opposite corners. Thus we may have the *cis*-form $\left[\begin{smallmatrix} (1)\text{X} \\ (2)\text{X} \end{smallmatrix} \text{Co En}_2 \right]$ and the *trans*-form $\left[\begin{smallmatrix} (1)\text{X} \\ (6)\text{X} \end{smallmatrix} \text{Co En}_2 \right]$. This isomerism has been realized in numerous cases. In case $\text{X} = \text{NO}_2$, another form of isomerism is possible according to whether NO_2 represents the nitro or the nitrito group. Both of these possibilities are realized experimentally.

A third realized form of isomerism is called by Werner ionization-metamerism, as is found in two forms such as $\left[\begin{smallmatrix} \text{O}_2\text{N} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co En}_2 \right] \cdot \text{X}$ and $\left[\begin{smallmatrix} \text{O}_2\text{N} \\ \text{X} \end{smallmatrix} \text{Co En}_2 \right] \cdot \text{NO}_2$, where $\text{X} = \text{Cl}, \text{Br}, \text{SCN}$, etc. Again in coördination-polymerism we have the nitrito-cobaltites of two different bases, $(\text{Co En}_2) \cdot \text{Co}(\text{NO}_2)_6$ and $\left[\begin{smallmatrix} \text{O}_2\text{N} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co En}_2 \right]_3 \cdot \text{Co}(\text{NO}_2)_6$, which are polymers. But yet more remarkable is the possibility of a fifth kind of isomerism. If the formula of the coördinated group $\left[\begin{smallmatrix} (1)\text{O}_2\text{N} \\ (2)\text{O}_2\text{N} \end{smallmatrix} \text{Co En}_2 \right]$ is really represented by the figure of an octahedron, it follows that there should be two forms which should be mirror images of each other, and from the analogy of compounds with an asymmetrical carbon compound, these should be optically active. This compound, as well as several others of similar type, have been prepared and have proved to be racemic compounds. They have been split into their active components by a method familiar in organic chemistry, namely, obtaining their campho-sulfonates or bromo-campho-sulfonates. The optical isomers show themselves to be actually optically active, and the two isomers have approximately the same but opposite rotation. What is true of cobalt bases, if representing a general principle, should be true of other similar bases, and therefore Werner attempted to apply it to the chromium ethylenediamine bases. Here he found in chromium dichloro-ethylenediamine chloride, $(\text{Cl}_2\text{Cr En}_2)\text{Cl}$, (chromium violeochloride) a racemic compound, which was broken up into its optically active components by bromo-campho-sulfonate, showing itself in every way analogous to the cobalt racemates. The chromium compounds have a smaller rotation than the corresponding compounds of cobalt. This brief summary will suffice to show the far-reaching character of Werner's recent work. If full justification for the old valence theory is found in the development which through it organic chemistry was enabled to make, certainly Werner's theory is well justified by the order it has already brought into the field of the complex compounds of inorganic chemistry. In this connection mention should be made of the work of Rosenheim (*Ibid.*, p. 1865) on the nitrito-cobaltites (cobalti-nitrites). Some time since, Hofmann and Buchner prepared a salt with the anion $\text{Co}(\text{OH})_3(\text{NO}_2)_3$, which should show stereoisomerism, according as to whether three similar groups are at the three corners of one face of the octahedron or not. By treating $\text{Na}_3\text{Co}(\text{NO}_2)_6$ with guanidium carbonate, there crystallize out at ordinary temperature large garnet-red crystals of $(\text{CN}_3\text{H}_3)_3 \cdot (\text{Co}(\text{OH})_3(\text{NO}_2)_3)$. From the mother liquor are obtained dark brick-red needles of the same composition, but which differ in solubility and in various precipitation reactions. In all probability they are the two stereoisomers called for by theory. Numerous other salts of the trihydroxy-trinitrito series were prepared, as well as the strontium salt of the dihydroxy-tetranitrito series. By the action of metal acetylacetonates on the hexanitrito salt a series of diacetylacetonodinitrito compounds was formed, where the coördinated group contains four negative groups, $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NO}_2)_2$.

In his investigations upon platinum Wöhler (*Z. Chem. Ind. Kolloide*, 7, 243) has found the most sensitive reagent for platinum to be SnCl_2 , which gives a red coloration to the solution unless very dilute, in which

case the color is yellow. In this way it is possible to detect 10^{-7} grams platinum in 1 cc. solution. This coloration is due to colloidal platinum, which is held in this condition by the presence of protective colloids resulting from the hydrolysis of SnCl_2 . It can also be produced by other reducing agents, as with ethereal phosphorus, in the presence of gelatin as protective colloid. On standing it goes over into a coarse brown colloid. The chocolate-brown precipitate in the red solution by the presence of the hydrolytic products of the SnCl_4 formed in the reaction is not a compound, but a mixture of platinum metal with stannic acid, analogous to the gold purple of Cassius. It is soluble (as appears to be the case with purple of Cassius) in acetic ester and in ether. With the bromides of platinum, stannous bromide causes a similar reaction. Wöhler also finds that the red coloration formed when stannous nitrate is added to silver nitrate (Ditte's reaction) is due to the formation of an analogous silver "purple."

In connection with the work of Gutbier, already mentioned, he has prepared a large number hexachloroplatinates, ruthenates and osmates, and hexabromoplatinates, of organic bases, both of the aliphatic and aromatic series (*Ber.*, 43, 3228, 3234; 44, 306, 308). The hexachlororuthenates are not formed by double decomposition from the alkali salts, as is the case with compounds of this type from the other platinum metals, but are formed by the interaction of the organic base, the pentachlororuthenite (M', RuCl_5) and chlorine. On the other hand the alkali salts of the hexachlororuthenate (M', RuCl_6) cannot be formed directly from the pentachlororuthenite by the action of chlorine or any other oxidizing agent. The explanation of this anomaly appears to the writer to rest in the fact that in the presence of organic substances the pentachlororuthenites are converted into the aquopentachlororuthenates, $\text{M}', \text{Ru}(\text{H}_2\text{O})\text{Cl}_5$, and that by the action of chlorine the water in these last salts is exchanged for Cl, giving the normal hexa-salts. This explains why the earlier workers on these salts, especially Claus and Joly, failed to prepare the hexachlororuthenates. Gutbier's success in preparing the hexachlororuthenates, so many of which he has described, is due to the fact that in the presence of the organic bases with which he worked, the penta-salt was converted into the aquopenta-salt, which readily unites with chlorine, giving the hexa-salts. Several additional papers have appeared from Delépine (*Compt. rend.*, 151, 878; 152, 1390, 1589; 153, 60; *Bull. soc. chim.*, [4] 9, 710, 771) on irido-disulfates, especially in connection with the action of pyridine. Unlike the stronger bases, pyridine seems to have no action on the iridodisulfates, but on standing, or more rapidly by heating, there takes place an externally almost unnoticeable change, resulting in the formation of a salt of pyridino-irido-disulfuric acid, $((\text{SO}_4)_2.\text{Ir}(\text{C}_5\text{H}_5\text{N})\text{OH}).\text{H}_2$. This forms crystalline salts with many inorganic bases; in these salts not all the cationic hydrogen is replaced, as is also the case with the original irido-disulfuric acid. Pyridine is found further to react with the aquopentachloroiridates, $\text{M}', \text{Ir}(\text{H}_2\text{O})\text{Cl}_5$, the water being replaced by pyridine, giving pyridino-chloroiridates, $\text{M}', \text{Ir}(\text{C}_5\text{H}_5\text{N})\text{Cl}_5$. With the hexachloroiridites, M', IrCl_6 , the same compound is formed, in this case one chlorine atom being replaced and the valence of the coördinated group reduced from three to two. If the solution obtained by the action of chlorine on ammonium hexachloroiridate, $(\text{NH}_4)_2\text{IrCl}_6$, is evaporated, a black deliquescent crystal-

line mass is obtained, $\text{H}_2\text{IrCl}_6 + 6\text{H}_2\text{O}$. On slow heating this loses both water and HCl , but it was not found possible to obtain either IrCl_4 or IrCl_3 . Further work on iridium has been done by Duffour (*Compt. rend.*, 152, 1393, 1591). By treating sodium hexachloroiridate with sodium oxalate, the oxalato-tetrachloroiridite, $\text{Na}_3\text{IrCl}_4(\text{C}_2\text{O}_4)_2$, is formed. On treating the silver salt with HCl , the free acid is obtained. On heating, this decomposes into tetrachloroiridous acid, H.IrCl_4 , of which several salts were formed. From the silver salt of tri-oxalatoiridous acid by HCl the free acid is formed, which gradually, by reversible reaction, goes over into diaquo-dioxalatoiridous acid, $\text{H}_3\text{Ir}(\text{C}_2\text{O}_4)_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{H.Ir}(\text{H}_2\text{O})_2 \cdot (\text{C}_2\text{O}_4)_2 + \text{H}_2\text{C}_2\text{O}_4$. From the potassium salt by the action of KOH there is formed a hydroxy-aquo salt, $\text{K}_2\text{Ir}(\text{OH})(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2$. On half neutralizing the free acid from this salt by KOH there is obtained an acid salt, $\text{KH.Ir}(\text{OH})(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2$, which is an isomer of the potassium salt of the (monobasic) diaquo salt, $\text{K.Ir}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2$, above.

The fact that the best determinations of the atomic weight of argon place it above that of potassium instead of below, as seems to be required by the periodic system, has led many to believe that ordinary argon contains similar elements of higher atomic weight. Fischer and Froboese (*Ber.*, 44, 92) have tried to solve the problem by the fractional crystallization of argon, using liquid air of different compositions as cooling agent, and an apparatus of their own devising for separating the crystals from the mother liquor. They find, however, no sign of resolution of argon into components, all fractions having the same density, representing the atomic weight of 39.9.

No attempt can be made here to review the work that has been done the past year on the radioactive elements, except to note that radium emanation, under the name of niton (Nt), has taken its place with some definiteness in Group VIII as the highest member of the He, Ne, Ar, Kr, Xe series, with an atomic weight of 223, and to call attention to two cases of the influence of niton, the one on atomic and the other on molecular reaction. In 1909 Ramsay announced that by the action of radium emanation on a solution of thorium, carbon dioxide appeared to be formed and that it seemed possible that under this influence carbon was a decomposition product of thorium. This was called in question by Herschfinkel (*Compt. rend.*, 153, 255), who on repeating Ramsay's experiments failed to get the same results, and attributed the carbon dioxide to the presence of oxalic acid in Ramsay's thorium. The latter has again described his work (*Ibid.*, p. 373) and the precautions taken. No oxalic acid could have been present; thorium nitrate without niton gave no CO_2 , nor did bismuth, mercury or silver nitrate under the same conditions give with niton any CO_2 . It seems probable therefore that the carbon actually arose from the decomposition of thorium under the influence of niton. The other case is a study by Lind (*Le Radium*, 8, 289) of the influence of radium upon the equilibrium $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$. No decomposition of hydrogen bromide could be detected in 37 days, but in the system H_2, Br_2 , in 14 days 2.6% of HBr had been formed. It is obviously impossible, starting from a definite amount of niton, to reach an equilibrium, since the decomposition of the niton has a higher velocity than that of the chemical reaction. No acceleration of the reaction due to the niton could be detected at higher temperatures. The decomposition of anhydrous liquid HBr , on the other hand, was decidedly hastened.

Aqueous solutions, both of the acid and of its salts, were rapidly decomposed by the emanation, the concentrated more rapidly than the dilute, but the increased velocity was not proportional to the concentration and is clearly influenced by secondary reactions.

In conclusion, allusion should be made to three new attempts to prepare periodic tables which shall prove more satisfactory than that of Mendeléeff, or others now in use. These are respectively by Schmidt (*Z. physik. Chem.*, 75, 651), Emerson (*Am. Chem. J.*, 45, 160) who proposes a "Helix chemica," and Van den Broek (*Physik. Ztschr.*, 12, 490), in whose table each group has three series instead of two, and which is based on "ideal" atomic weights, which often differ to the extent of several units from those which have been experimentally determined.

WASHINGTON AND LEE UNIVERSITY.
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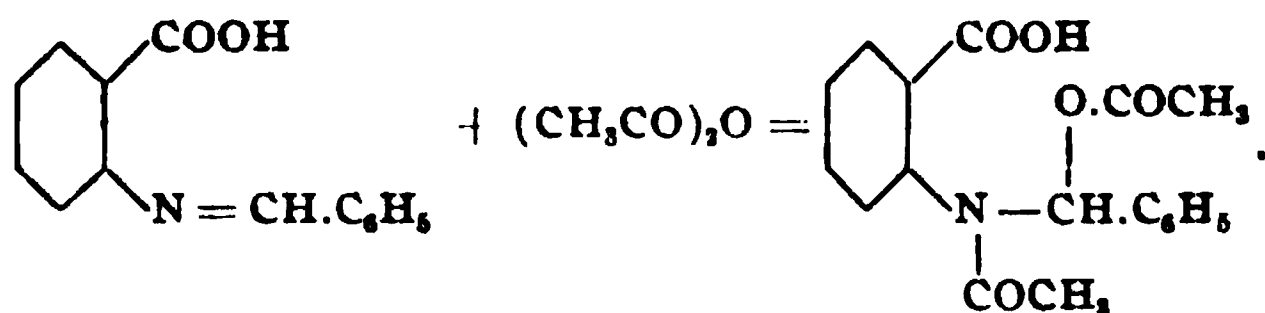
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]

THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS.

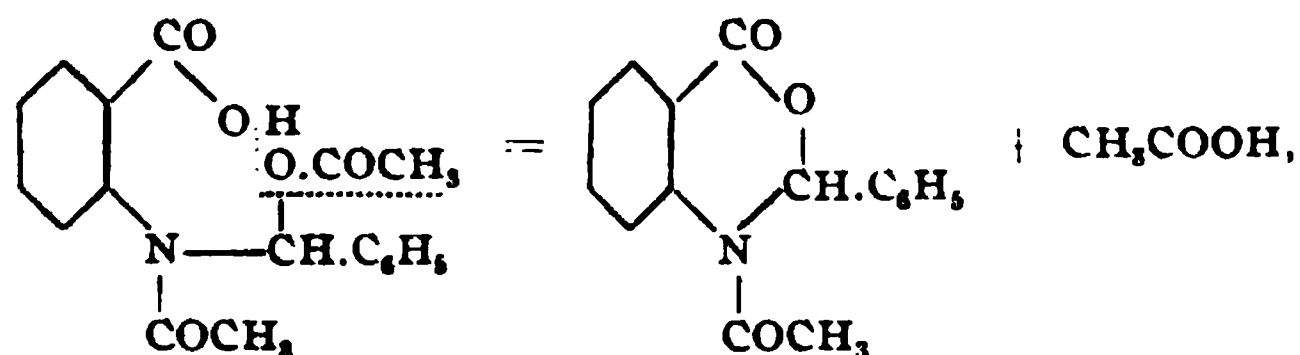
BY JOHN B. EEELEY AND PAUL M. DEAN.

Received November 21, 1911.

Anthranilic acid reacts with aromatic aldehydes with the formation of benzylidene derivatives. These derivatives react with acetic anhydride, giving a series of oxazines. The reaction probably passes through an intermediate stage in which a molecule of the benzylidene derivative adds a molecule of acetic anhydride thus:



Heating splits off a molecule of acetic acid thus,



giving an acetketodihydrobenzmetoxazine.¹

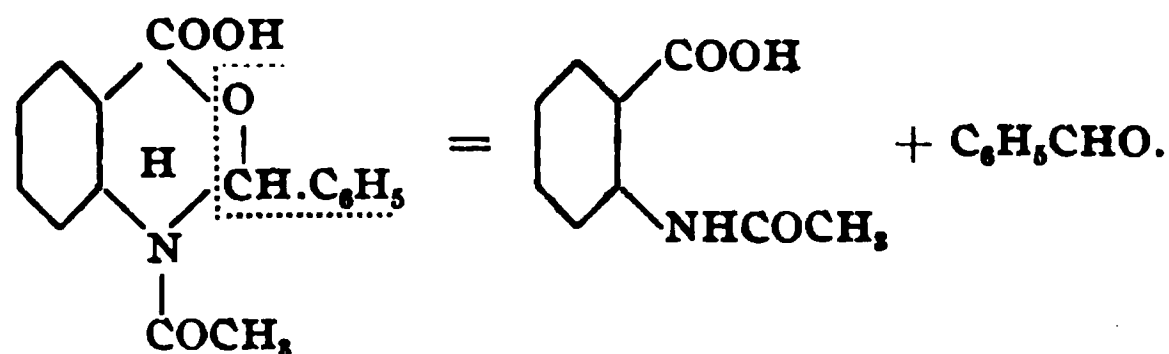
The reaction seems to be general, since in the cases thus far studied with aromatic aldehydes, the condensation takes place with ease. This paper will deal with the oxazines obtained from benzylidene, metanitrobenzylidene, paranitrobenzylidene, paraoxybenzylidene, salicylidene, and vanillylidene anthranilic acids. These oxazines are colorless,

¹ The Badische Anilin und Soda Fabrik has patented a process for making a series of compounds containing the metoxazine ring, abstracts of which are given in the *Chem. Zentralblatt*, 1910, I, 308, 309, 1564; 1911, I, 853.

crystallin solids, with the exception of the one from vanillin, which is straw colored, and are very stable, requiring boiling with acids or alkalis to affect decomposition. The compounds obtained from meta- and paranitrobenzylidene anthranilic acid may be boiled with concentrated sodium hydroxide with only slight decomposition.

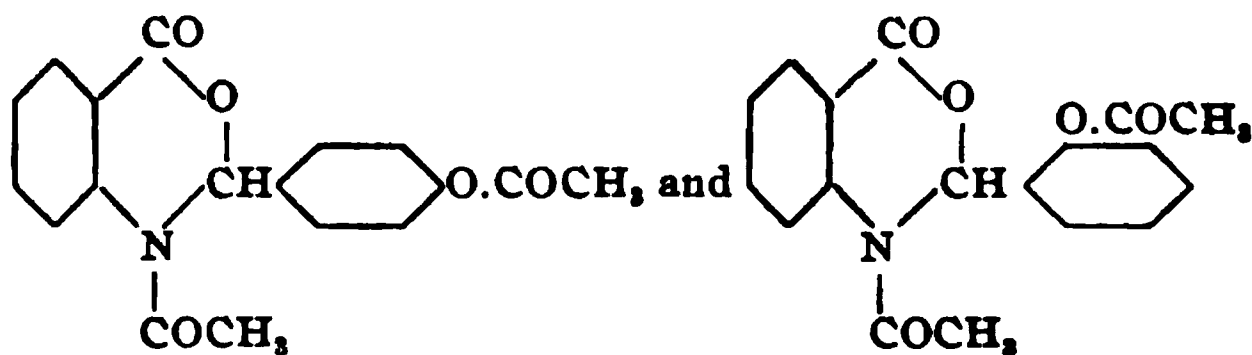
Just as this paper was being finished, we noted an abstract of a paper by Wolf,¹ in which he describes the benzylidene derivatives (except that from vanillin) from which we have made our condensation products. Since the methods of preparation are different, we are also including them in this paper.

The constitution of the condensation product from benzylidene anthranilic acid and acetic anhydride was proved from the decomposition products obtained when it was heated with strong hydrochloric acid. Benzaldehyde was given off and a crystallin substance separated out, which proved to be acetanthranilic acid, melting at 185°. The decomposition evidently takes place as follows:



The compound therefore is phenylacetketodihydrobenzmetoxazine.

In the condensation products from *p*-hydroxybenzylidene and salicylidene anthranilic acids, it was found that the hydrogen of the hydroxyl group had been replaced by acetyl, thus:



Experimental Part.

Benzylidene Anthranilic Acid.—One gram-molecule of anthranilic acid in benzene solution was heated with 1 gram-molecule of benzaldehyde under reflux on the water bath. A little animal charcoal was added, and the solution filtered. Light straw-colored needles separated out on cooling. These were contaminated with a small amount of anthranilic acid, so that several recrystallizations from benzene were necessary to obtain the substance pure. Melting point, 126°.

Calculated for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: N, 6.22. Found, 6.52.

Phenylacetketodihydrobenzmetoxazine.—Benzylidene anthranilic acid was heated in an Erlenmeyer flask with an excess of acetic anhydride for 4

¹ *Monatsheft*, 31, 903-16.

hours on the water bath. By means of a bent glass tube connected with a suction pump, the vapors of acetic anhydride were drawn off from the solution, while still on the water bath, until it was sufficiently concentrated to allow the oxazine to crystallize out. On cooling the flask, the contents solidified. The crystals were filtered off, pressed out on a porous plate, and recrystallized from methyl alcohol. Colorless prisms, soluble in the ordinary organic solvents. Melting point 108° .

Calculated for $C_{16}H_{13}NO_3$: N, 5.24; C, 71.91; H, 4.87.

Found: N, 5.50; C, 71.80; H, 4.78.

m-Nitrobenzylidene Anthranilic Acid.—One gram-molecule of anthranilic acid was dissolved in just enough alcohol to hold it in solution when placed in a freezing mixture of ice and salt. One gram-molecule of pulverized *m*-nitrobenzaldehyde was then added with constant stirring of the solution. In a short time, the *m*-nitrobenzylidene anthranilic acid separated out, so that the contents of the beaker became solid. The crystals were filtered off by suction, pressed out on a porous plate, and recrystallized from alcohol. Light straw-colored needles, soluble in the usual organic solvents. Melting point, 202° .

Calculated for $C_{14}H_{10}N_2O_4$: N, 10.37. Found, 10.76.

m-Nitrophenylacetketodihydrobenzmetoxazine. — One gram-molecule of metanitrobenzylidene anthranilic acid was heated with an excess of acetic anhydride on the water bath, until, in a short time, the oxazine crystallized out. The crystals were filtered off by suction, and washed with alcohol and then ether to remove the excess acetic anhydride. The substance was recrystallized from boiling xylene. Thick, colorless crystals, insoluble in the ordinary organic solvents, soluble in hot xylene. Melting point, 192° .

Calculated for $C_{16}H_{13}N_2O_5$: N, 8.98; C, 61.51; H, 3.80.

Found: N, 9.05; C, 61.30; H, 3.98.

p-Nitrobenzylidene Anthranilic Acid.—*p*-Nitrobenzylidene anthranilic acid was prepared in the same manner as the corresponding *meta* product. Straw-colored needles, soluble in the ordinary organic solvents. Melting point, 164° .

Calculated for $C_{14}H_{10}N_2O_4$: N, 10.37. Found, 10.68.

p-Nitrophenylacetketodihydrobenzmetoxazine.—This oxazine was prepared in exactly the same manner as that from metabenzylidene anthranilic acid. The oxazine crystallized out from the acetic anhydride solution in silky white needles, which were filtered off by suction, washed with alcohol and then with ether, after which treatment they were found to be pure. Insoluble in the ordinary organic solvents. Soluble in hot xylol. Melting point, 199° .

Calculated for $C_{16}H_{13}N_2O_5$: N, 8.98; C, 61.51; H, 3.80.

Found: N, 9.19; C, 61.46; H, 4.10.

p-Oxybenzylidene Anthranilic Acid.—*p*-Oxybenzylidene anthranilic acid was made in alcoholic solution in the same way as the *p*-nitro compound. This substance crystallized out in the form of lemon-yellow needles. Soluble in the ordinary organic solvents. Melting point, 207°.

Calculated for $C_{14}H_{11}NO_3$: N, 5.80. Found, 5.98.

Acetyl-p-oxyphenylacetketodihydrobenzmetoxazine.—This compound was made in exactly the same way as the preceding oxazines. In this case the hydrogen of the hydroxyl group is replaced by acetyl. Recrystallized from methyl alcohol, it yields colorless prisms. Melting point, 148°.

Calculated for $C_{18}H_{15}NO_3$: N, 4.31; C, 66.46; H, 4.61.

Found: N, 4.68; C, 66.11; H, 4.94.

Salicylidene Anthranilic Acid.—Salicylidene anthranilic acid was prepared in a manner analogous to that of the other benzylidene products. Orange-red crystals from alcohol. Soluble in ordinary organic solvents. Melting point, 195°.

Calculated for $C_{14}H_{11}NO_3$: N, 5.81. Found, 6.03.

Acetyl-o-oxyphenylacetketodihydrobenzmetoxazine.—This compound was prepared from salicylidene anthranilic acid in the same way as the preceding oxazines. Colorless crystals from methyl alcohol. Melting point, 162°.

Calculated for $C_{18}H_{15}NO_3$: N, 4.31; C, 66.46; H, 4.61.

Found: N, 4.64; C, 65.85; H, 4.75.

Vanillylidene Anthranilic Acid.—Equimolecular solutions of anthranilic acid and vanillin in benzene were mixed. On standing, lemon-yellow needles crystallized out. Recrystallization from boiling benzene yielded a product melting at 170°.

Calculated for $C_{15}H_{13}NO_4$: N, 5.16. Found, 5.01.

3-Methoxy-4-oxyphenylacetketodihydrobenzmetoxazine.—This compound was prepared from vanillylidene anthranilic acid and acetic anhydride in the same manner as the preceding oxazines. Light straw-colored crystals, melting at 184°.

Calculated for $C_{19}H_{17}NO_6$: N, 3.94; C, 64.22; H, 4.78.

Found: N, 4.19; C, 63.94; H, 5.02.

Condensation products from other benzylidene anthranilic acids are being prepared and will be described in a succeeding paper.

BOULDER, COLORADO.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]
THE ACTION OF ALCOHOLATES AND AMINES ON BENZOYLISOCYANCHLORIDE.

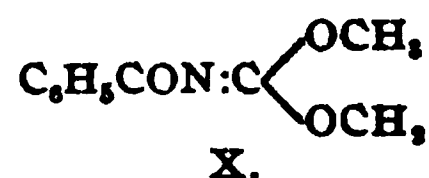
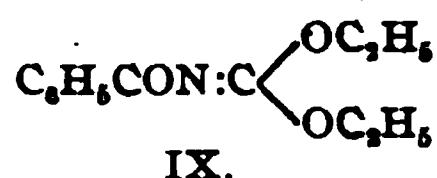
BY TREAT B. JOHNSON AND LEWIS H. CHERNOFF.

Received December 1, 1911.

Of the three classes of acylimidocarbonates, I, II and III, only the

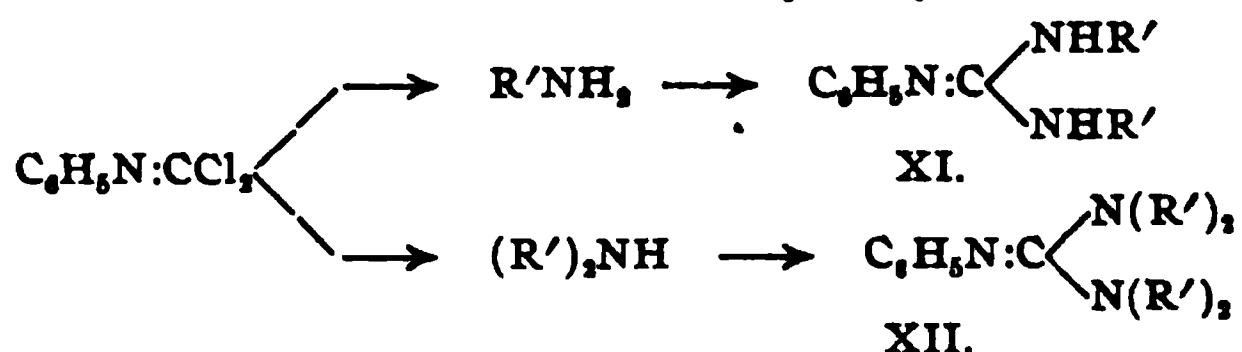
ever, if protected from moisture in tightly stoppered bottles, it can be preserved for months without decomposition.

Benzoylisocyanchloride, VIII, combines with sodium alcoholates, forming representatives of the hitherto unknown class of *acylimidocarbonates*, I. We have prepared for examination only two members of this series, *viz.*, diethyl- and dimethylbenzoylimidocarbonates, IX and X. They were formed by the action of sodium ethylate and sodium

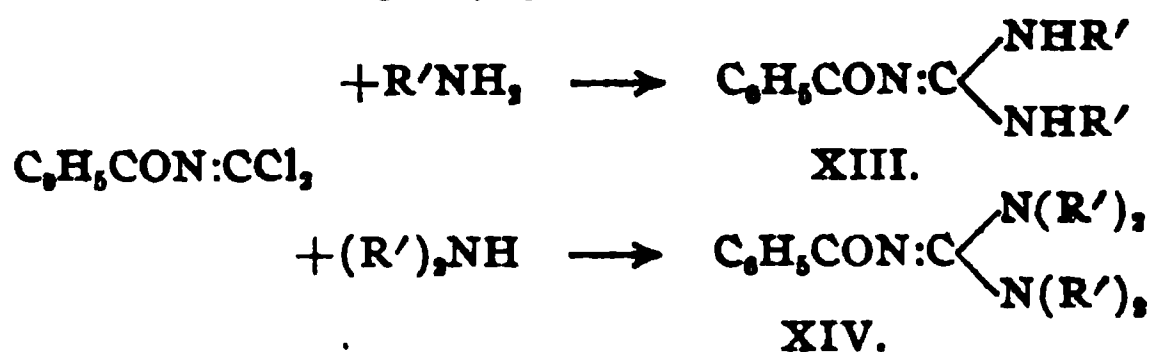


methylate respectively on the chloride. These esters were obtained as colorless oils of remarkable stability and could be distilled without decomposition. They undergo hydrolysis when warmed with alkali and hydrochloric acid, forming benzoic acid. The most characteristic property of this type of compounds was their remarkable stability when heated with organic bases. The acylimidothio- and acylimidodithiocarbonates, II and III, combine easily with amines, forming acylpseudo-ureas and acylpseudothioureas, respectively, with evolution of mercaptans.¹ Diethyl benzoylimidocarbonate, on the other hand, showed no tendency to react with aniline when heated with this reagent at 160°. There was no evidence of the formation of benzoylphenylpseudoethylurea. The same inertness was also manifested when the ester was heated with phenylhydrazine.

Phenylisocyanchloride reacts with amines giving tri- and penta-substituted guanidines,² XI and XII. Benzoylisocyanchloride reacts with



bases, in a perfectly similar manner, forming practically quantitative yields of the corresponding acylguanidines as follows:

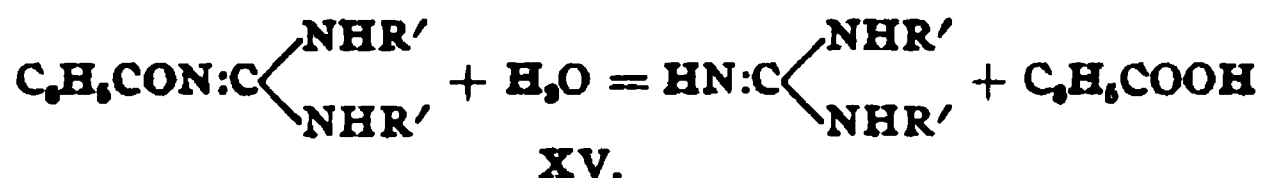


These acylguanidines, XIII and XIV, possess basic properties and form stable salts with mineral acids. When digested with alkali they undergo hydrolysis with formation of the free guanidines, XV, and benzoic acid.

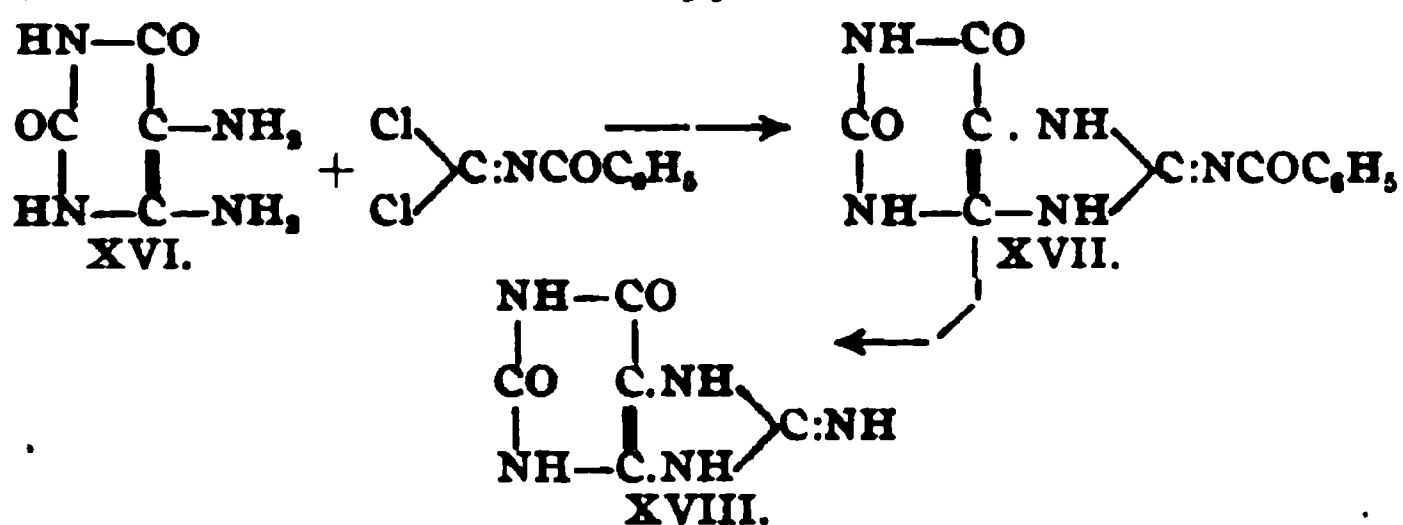
¹ Wheeler and Johnson, *loc. cit.*

² *Loc. cit.*

In fact, the yield of the guanidine base is excellent and with an accessible chloride like benzoylisocyanchloride we have a new simple method of preparing guanidines of these types easily and in any amount desired.



Benzoylisocyanchloride should be of value for the synthesis of 8-amino-purines, XVIII, from orthodiaminopyrimidines, XVI.



Experimental Part.

The benzoylisothiocyanate,¹ $\text{C}_6\text{H}_5\text{CONCS}$, which was used in this investigation, was prepared by the action of benzoylchloride on lead thiocyanate. The lead salt was made by dissolving lead acetate in water and then precipitating the thiocyanate by addition of the required amount of potassium thiocyanate. After filtering and washing with water and alcohol, the salt was then thoroughly dried in a desiccator over concentrated sulfuric acid. For the preparation of the rhodanide, 65 grams of the thiocyanate were suspended in 100 cc. of dry benzene, 55 grams of benzoylchloride added and the mixture was digested in an oil bath at $110-120^\circ$ for one hour. The yield of rhodanide is diminished by too long digestion and by heating at a higher temperature. After cooling, the lead chloride and excess of lead thiocyanate were separated by filtration, the excess of benzene evaporated in a partial vacuum and the rhodanide then purified by distillation under diminished pressure. The yield of pure rhodanide was 30 grams.

Benzoylisocyanchloride, $\text{C}_6\text{H}_5\text{CONCCl}_2$.—This compound has been described in a previous publication from this laboratory.² It was prepared by the action of chlorine on benzoylisothiocyanate in chloroform solution. We now find that it is formed far more smoothly by chlorination of the isothiocyanate when dissolved in carbontetrachloride. Thirty grams of benzoylisothiocyanate are dissolved in at least 3 volumes of anhydrous carbontetrachloride and the flask connected by a 3-way tube with a return condenser. The flask is then connected with a chlorine bomb and chlorine passed into the solution at 0° for 4 hours and the

¹ Miquel, *Ann. chim. phys.*, [5] 11, 300.

² Johnson and Menge, *loc. cit.*

solution then allowed to stand for 2–3 days. Under these conditions a red liquid is obtained in which is usually suspended a small amount of amorphous material. After filtering, the excess of carbontetrachloride and sulfur chloride is then evaporated in a vacuum and the isocyanchloride finally purified by distillation under diminished pressure. The yield was 25.0 grams. This yield, however, is greatly diminished if precautions are not taken throughout the experiment to exclude all moisture. The chloride obtained in 4 different experiments distilled as follows: 150–160° at 20–30 mm., 170–175° at 53 mm., 178–185° at 56 mm. and 115–121° at 20 mm.

Diethyl Benzoylimidocarbonate, $C_6H_5CON : C \begin{matrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}$.—This ester was

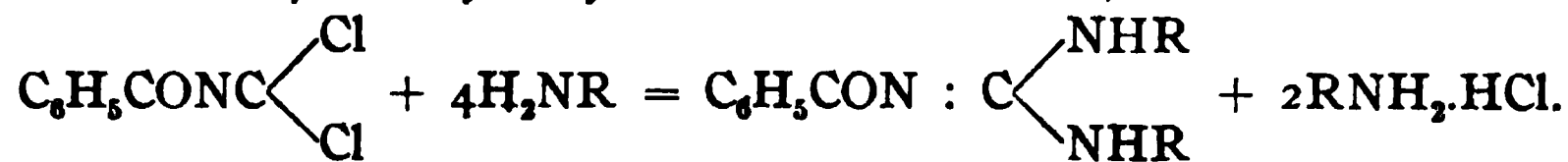
prepared by the action of benzoylisocyanchloride on sodium ethylate. Four and six-tenths grams of sodium were converted into dry sodium ethylate and the latter suspended in 200–300 cc. of anhydrous ether. The required amount of benzoylisocyanchloride was then carefully added and the mixture digested on the steam bath until the pungent odor of the isocyanchloride entirely disappeared (6–8 hours). After filtering from sodium chloride, the ether was evaporated and the carbonate distilled under diminished pressure. It boiled at 93–100° under 20 mm. pressure and at 110–120° under 32 mm. pressure. Analysis (Kjeldahl):

Calculated for $C_{15}H_{18}O_3N$: N, 6.31. Found, 6.5.

Dimethyl Benzoylimidocarbonate, $C_6H_5CON : C(OCH_3)_2$, was prepared in a similar manner as the above ethyl ester by the action of the isocyanchloride on dry sodiummethylete. It was obtained as a colorless oil, which distilled at 95–102° at 20 mm. pressure.

Hydrolysis of Diethyl Benzoylimidocarbonate with Alkali.—One gram of the ester was warmed, on the steam bath, with 50 cc. of a 10% potassium hydroxide solution until it dissolved. After cooling and acidifying with hydrochloric acid, pure benzoic acid separated and melted at 120°.

The Action of Benzoylisocyanchloride on Amines,



—This chloride reacts violently with bases forming the benzoyl derivatives of dialkyl guanidines. Dilution of the reagents with an inert solvent is necessary in order to obtain smooth reactions. The general procedure was to dissolve the base in dry benzene and then add this solution cautiously to a benzene solution of the chloride. There was usually an immediate reaction, with evolution of much heat and the free acylguanidine and, in some cases, its hydrochloride separated at once in crystalline form. After digestion for 2–3 hours to complete the reaction the benzene

was evaporated and the compound purified by recrystallization from a suitable solvent.

1,3-Diphenyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_5)_2$.—This compound was prepared by dissolving 9.2 grams of aniline in 30 cc. of benzene and adding slowly to a solution of 5.0 grams of benzoylisocyanchloride in 50 cc. of benzene. After warming 4.5 hours on the steam bath and cooling, an insoluble, colorless, crystalline substance was obtained. This was identified as a mixture of aniline hydrochloride and the hydrochloride of the acylguanidine. This material was washed with cold water to remove the aniline hydrochloride and the hydrochloride of the acylguanidine purified by crystallization from 95% alcohol. It separated, on cooling, in needles, which melted at 212° with decomposition.

Nitrogen (Kjeldahl)—Calculated for $C_{20}H_{17}ON_3 \cdot HCl$: N, 11.90. Found, 11.70.

The benzene filtrate above was concentrated and cooled, when the free guanidine deposited. It dissolved in boiling 95% alcohol and separated on cooling in prisms, which melted at 104° to an oil. Analysis (Kjeldahl):

Calculated for $C_{20}H_{17}ON_3$: N, 13.33. Found, 13.30.

Hydrolysis of 1,3-Diphenyl-2-benzoylguanidine.—This guanidine is very stable in the presence of hydrochloric acid. Three grams of the base were digested with 50 cc. of dilute hydrochloric acid for 2 hours and the solution then evaporated to dryness. On crystallizing the residue from 95% alcohol the hydrochloride of the unaltered benzoylguanidine was obtained and it melted at $209-210^\circ$ with effervescence. One and five-tenths grams of the benzoylguanidine were digested with 50 cc. of a 15% solution of potassium hydroxide for 2 hours and the solution then evaporated to dryness. The residue obtained was then triturated with cold water to remove the alkali and the undissolved material purified by crystallization from boiling 95% alcohol. On cooling, diphenylguanidine separated and melted at $146-148^\circ$.

Calculated for $C_{12}H_{11}N_3$: N, 19.90. Found, 19.81.

1,3-Di-o-tolyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4CH_3)_2$.—From orthotoluidine and benzoylisocyanchloride. It crystallized from 95% alcohol in flat prisms, which melted at 126° .

Calculated for $C_{22}H_{21}ON_3$: N, 12.24. Found, 11.84.

1,3-Di-m-tolyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4CH_3)_2$.—From m-toluidine and benzoylisocyanchloride. It is soluble in boiling benzene and separates from a hot 95% alcohol solution in needles, which melt at $177-178^\circ$.

Calculated for $C_{22}H_{21}ON_3$: N, 12.24. Found, 12.30.

Di-m-tolylguanidine, $HN : C(NHC_6H_4CH_3)_2$.—A quantitative yield of this base was obtained by hydrolysis of the preceding benzoyl derivative

with potassium hydroxide. It was purified by crystallization from 95% alcohol and melted at 108–109° to a clear oil.

Calculated for $C_{15}H_{14}N_2$: N, 17.56. Found, 17.71.

1,3-Di-p-tolyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4CH_3)_2$.—From *p*-toluidine and benzoylisocyanchloride. It crystallized from benzene in rhombic prisms, which melted at 190°.

Calculated for $C_{22}H_{21}ON_2$: N, 12.24. Found, 12.40.

Hydrochloride, $C_{22}H_{21}ON_2 \cdot 2HCl$.—This salt is very soluble in alcohol and crystallizes from benzene in prisms, which melt at 190–191° with decomposition.

Calculated for $C_{22}H_{21}ON_2 \cdot 2HCl$: N, 10.09. Found, 10.01.

Benzoyltetraphenylguanidine, $C_6H_5CON : C[N(C_6H_5)_2]_2$.—From diphenylamine and benzoylisocyanchloride. This was obtained as a colorless solid which crystallized from 95% alcohol in prismatic crystals. It melted at 142–144°.

Calculated for $C_{28}H_{25}ON_2$: N, 8.99. Found, 8.66.

1,3-Dimethyl-1,3-diphenyl-2-benzoylguanidine, $C_6H_5CON : C[N(CH_3)C_6H_5]_2$.—From monomethylaniline and benzoylisocyanchloride. It crystallized from 95% alcohol in well-developed rhombic prisms, which melted at 135°.

Calculated for $C_{22}H_{21}ON_2$: N, 12.24. Found, 12.00.

1,3-Di-p-anisyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4OCH_3)_2$.—From paraanisidine and benzoylisocyanchloride. It crystallized from alcohol in needles, which melted at 128° to an oil.

Calculated for $C_{23}H_{21}O_2N_2$: N, 11.20. Found, 11.09.

Di-p-anisylguanidine, $HN : C(NHC_6H_4OCH_3)_2$.—Separated from hot alcohol in flakes, which melted at 153°.

Calculated for $C_{18}H_{17}O_2N_2$: N, 14.91. Found, 14.87.

1,3-Di-β-naphthyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_{10}H_7)_2$.—From β-naphthylamine and benzoylisocyanchloride. This base crystallized from alcohol in prisms, which melted at 162°.

Calculated for $C_{28}H_{21}ON_2$: N, 10.07. Found, 10.04.

Di-β-naphthylguanidine, $HN : C(NHC_{10}H_7)_2$.—A quantitative yield of this guanidine is obtained by hydrolysis of the above benzoyl compound. It melted at 197°, with slight effervescence.

Calculated for $C_{24}H_{17}N_2$: N, 13.50. Found, 13.61.

NEW HAVEN, CONN., Nov. 28, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

2,2,3-TRIMETHYLPENTANE.

BY LATHAM CLARKE AND WEBSTER NEWTON JONES.

Received December 2, 1911.

The hydrocarbons of the formula C_8H_{18} have been a subject of study

in this laboratory for some years,¹ and in furtherance of this study, the synthesis and determination of the properties of 2,2,3-trimethylpentane, $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, have been taken up. This octane is the first to be made in this laboratory, containing a quaternary carbon atom. But one other octane containing a quaternary carbon atom has hitherto been synthesized and that is 2,2,3,3-tetramethylbutane, or hexamethyl ethane, which contains two quaternary carbon atoms and was prepared by Henry.²

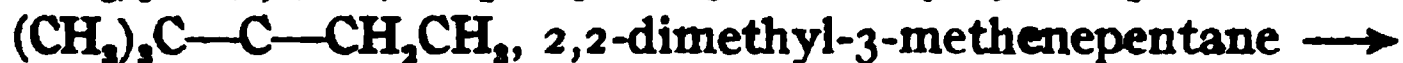
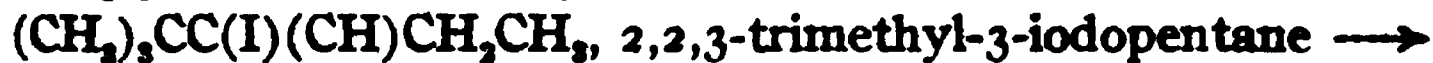
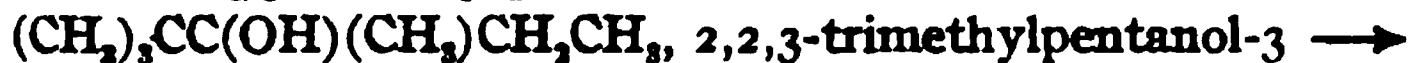
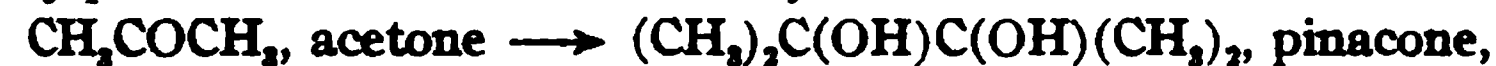
The literature records but three other paraffin hydrocarbons, with similar quaternary arrangements, viz., 2,2-dimethylpropane,³ 3,3-dimethylbutane⁴ and 3,3-dimethyl pentane.⁵

Like all the other octanes as yet synthesized in this laboratory, 2,2,3-trimethylpentane is a liquid. It boils at $110.5\text{--}110.8^\circ$ at 760 mm. pressure, and has at 15° the specific gravity 0.7219, compared to water at 15° . Henry's 2,2,3,3-tetramethylbutane was a solid, melting at $103\text{--}104^\circ$ and boiling at $106\text{--}107^\circ$ at 765 mm.

Special Theoretical.

The procedure which seemed most promising for the synthesis of 2,2,3-trimethylpentane and which was successfully carried out was as follows:

From acetone by reduction, pinacone was formed, and this by boiling with dilute sulfuric acid was rearranged to pinacolone. Since pinacolone is a ketone, it could be made to react with ethyl magnesium bromide producing a tertiary alcohol, 2,2,3-trimethylpentanol-3, which was converted into the corresponding carbinol iodide by means of red phosphorus and iodine. This carbinol iodide readily lost the elements of hydriodic acid on treatment with alcoholic potash, thereby producing 2,2-dimethyl-3-methene pentane, which by passing over finely divided nickel at 160° , in a current of hydrogen, was reduced to the desired octane, 2,2,3-trimethylpentane. These reactions may be summarized as follows:



¹ A résumé of the properties of normal octane, the three methylheptanes and the four dimethylhexanes is given in THIS JOURNAL, 33, 520, *et seq.* The description of another octane, 2-methyl-3-ethylpentane (or the old name, diethylisopropylmethane), not included in the list referred to, may be found as follows: *Am. Chem. J.*, 39, 574.

² *Compt. rend.*, 142, 1075 (1906).

³ Lewow, *Z.*, 1870, 520; 1871, 257.

⁴ Gorianow, *Ann.*, 165, 107.

⁵ Friedel, Ladenburg, *Ann.*, 142, 310.

Experimental Part.

In this research, acetone was reduced to pinacone by three methods: The first was the old procedure of Friedel and Silva,¹ using sodium in the presence of a strong solution of potassium carbonate, but this is applicable only on a small scale, and gives a small yield, about 10% of the theoretical. The second method was Richard and Langlais' Modification of Couturier and Meunier's process,² who employed magnesium amalgam as the reducing agent. This did not prove satisfactory on account of the difficulty of extracting the pinacone at the end of the process, so we took up the method of Holleman,³ and reduced the acetone with magnesium turnings in the presence of mercuric chloride. The last method was very satisfactory and with certain modifications which we introduced was carried on in the following manner:

One hundred and fifty grams of dry acetone containing 25 grams of mercuric chloride were gradually added to 25 grams of magnesium turnings contained in a liter flask, fitted with a return condenser. After the active reaction which began at first had apparently ceased, the mixture was heated for two hours on the steam bath. The quantitative amount of water (37.5 grams) was then introduced and the heating continued for an hour. An excess of water had to be carefully guarded against, as it formed a sort of emulsion which later prevented the extraction of the pinacone. Next the mixture was treated with 50 cc. of acetone and heated a few moments, then allowed to stand until the precipitate settled, when the supernatant acetone solution of pinacone was decanted, while to the residue fresh acetone was added, heated as before, settled, and the acetone extract once more poured off. This process of extraction was repeated several times or until the acetone extract was no longer colored red.

All the acetone solutions were placed together and fractionally distilled. The portion boiling between 150° and 180° was mixed with water and boiled, then cooled, whereby pinacone hydrate, $C_6H_{14}O_2 \cdot 6H_2O$, separated out and was recrystallized again from water. Thus the other substances formed in the reduction of the acetone were eliminated by the processes of distillation and crystallization and the pinacone hydrate was obtained in a pure state. The yield of the hydrate was usually 83 grams or 35% of the theoretical figures on the basis of the magnesium.

Pinacoline.—Although various acids may be used for the conversion of pinacone into pinacoline, we found that the most satisfactory was sulfuric acid of a strength of 5%. In a typical experiment, 200 grams of pinacone hydrate were mixed with 350 grams of 5% sulfuric acid and

¹ *Jarhesb.*, 1873, 340. Thiele, *Ber.*, 27, 455, suggests the use of caustic potash in place of potassium carbonate.

² *Bull. soc. chim.*, [4] 7, 454 (1910).

³ *Rec. trav. chim. Pays-Bas.*, 25, 206-7.

slowly distilled. The pinacoline collected in the receiver as a floating oily layer on the water, and was separated, dried with fused calcium chloride and distilled. The fraction taken for the next reaction boiled at 103–107°. The yield was 84 grams crude pinacoline, corresponding to 95% of the theoretical.

2,2,3-Trimethylpentanol-3, $(\text{CH}_3)_3\text{CC}(\text{OH})(\text{CH}_2)\text{CH}_2\text{CH}_3$.—This carbinol containing eight atoms of carbon was prepared from pinacoline, by the Barbier-Grignard reaction, using ethyl magnesium bromide. In a typical experiment, 18 grams of magnesium turnings were dissolved in 82 grams of ethyl bromide which had previously been diluted with an equal volume of anhydrous ether. To the solution, 50 grams of pinacoline, diluted with one volume of ether, were added and the mixture was allowed to stand two hours before decomposing in the usual manner with water and hydrochloric acid. The ether layer was removed and dried over potassium carbonate, after which the ether was distilled off, and the residue subjected to fractional distillation. After four fractionations, 34 grams of a liquid were obtained, boiling at 149–152° at 760 mm. pressure. This was 2,2,3-trimethylpentanol-3.

Calculated for $\text{C}_8\text{H}_{18}\text{O}$: C, 73.85; H, 13.60.

Found: C, 74.14; H, 13.85.

Properties: Colorless liquid boiling at 149–152° at 760 mm. pressure. It has an odor quite like that of camphor. It is immiscible with water but miscible with the common organic solvents.

2,2,3-Trimethyl-3-iodopentane, $(\text{CH}_3)_3\text{C}(\text{I})(\text{CH}_2)\text{CH}_2\text{CH}_3$.—In each experiment, 50 grams of 2,2,3-trimethyl-3-pentanol were mixed with 8 grams of red phosphorus and treated with 60 grams of iodine in small portions at a time, the temperature being maintained below 20°. At the end of an hour, the temperature was raised to 70°, at which point it was held 4 hours. After cooling, the mixture was filtered through glass wool to remove red phosphorus, washed with cold water and converted without further purification into the octylene.

2,2-Dimethyl-3-methenepentane, $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_2)\text{CH}_2\text{CH}_3$.—The octyl iodide



of the preceding paragraph was converted into 2,2-dimethyl-3-methenepentane by the following procedure: One hundred and seventy-three grams of octyl iodide were treated on a sand bath for four hours with a solution of 120 grams of potassium hydroxide in 600 cc. of alcohol. By replacing the return condenser with an ordinary condenser, the alcohol was distilled off and carried with it the octylene. Although the octylene boils slightly above 110°, with alcohol it forms a soluble binary mixture boiling at about 80°. By dilution of the alcohol with water, the octylene separated as a floating layer, which was removed and dried over calcium

chloride. The yield of crude octylene was 67 grams. This was fractionally distilled and finally yielded 25 grams of octylene boiling at 110.4–110.8° at 760 mm. pressure.

Calculated for C_8H_{16} : C, 85.71; H, 14.29.

Found: C, 85.49; 85.00; 84.72; H, 13.27; 13.50; 14.40.

Properties: Colorless, mobile liquid with a faint musty odor. Boiling point, 110.4–110.8° at 760 mm. pressure. It is not miscible with water, but mixes fairly readily with the common organic solvents.

2,2,3-Trimethylpentane, $(CH_3)_3CH(CH_2)CH_2CH_3$. — The octylene was reduced to the octane by Bedford's modification of Sabatier and Senderens' method,¹ by the action of hydrogen and pure nickel at 160–180°. From 12 grams of octylene, 8 grams of octane were obtained, boiling at 110.5–110.8° at 760 mm. pressure.

Calculated for C_8H_{18} : C, 84.21; H, 15.79.

Found: C, 84.56; 84.63; 83.64; H, 15.69; 15.60; 15.88.

Properties: Colorless, very mobile liquid, with a very faint odor. Boiling point, 110.5–110.8° at 760 mm. pressure. The specific gravity at 15° compared to water at 15° is 0.7219. The index of refraction was determined with a fine Pulfrich refractometer. $N_D(25^\circ) = 1.4164$.

CAMBRIDGE, MASS.

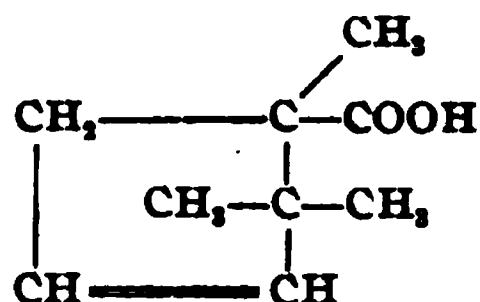
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IX.
LAURONOLIC ACID AND CAMPHOLACTONE.²

BY WILLIAM A. NOYES AND CHARLES E. BURKE.

Received June 26, 1911.

Two unsaturated acids derived from camphor, having the formula $C_{13}H_{19}COOH$, and having the carboxyl group in the tertiary position are known.

One of these has been isolated by Bredt³ and since on oxidation it gives camphoronic acid he has given to it the structure



The other acid was first studied by Fittig and Woringen.⁴ It has been obtained in two ways: first, by the decomposition of bromo-camphoric acid anhydride by boiling with water or with dilute alkali; second, by the

¹ The exact process is described by Clarke and Beggs in THIS JOURNAL, 34, 59.

² Abstract of a thesis presented by Charles E. Burke in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.

³ Ber., 35, 1286.

⁴ Ann., 227, 6.

distillation of camphanic acid, either alone or in a slow current of carbon dioxide.

Fittig and Woringer, and Aschan¹ assumed the acids obtained in these two ways to be identical, since they gave the same lactone, hydrobromide, amide and bromolactone. Tiemann² noticed that the two acids differed widely in their effect upon the rotation of polarized light and suggested that that obtained by the distillation of camphanic acid was probably a mixture of optical isomers, since its rotation varied from $+110^\circ$ to $+188^\circ$ while that obtained by the decomposition of the anhydride gave a constant rotation of $+199^\circ$ at 19° .

That the acid obtained by the distillation of camphanic acid is a mixture of optical isomers we have definitely shown by a comparison of the properties of three acids prepared in the following ways:

(A) By the decomposition of active bromocamphoric acid anhydride with sodium carbonate.

(B) By the distillation of camphanic acid.

(C) From inactive (artificial) camphor in the same way as (A) above.

For these acids the following properties have been observed:

ROTATION.

(A) From the active anhydride.

$$[\alpha]_D^{25} = +187.7^\circ$$

(B) From camphanic acid:

$$[\alpha]_D = +63^\circ \text{ to } +180^\circ$$

(C) From inactive camphor.

$$[\alpha]_D = 0^\circ$$

DENSITY.

$$D_4^{25} = 1.0133$$

$$D_4^{25} = 1.0227$$

$$D_4^{25} = 1.0318$$

VAPOR PRESSURE.

Temp. 184°
v. p. 100 mm.

Temp. 188°
v. p. 100 mm.

Temp. 193°
v. p. 100 mm.

INDEX OF REFRACTION.

D 1.47586
C 1.47269
F 1.48323
G 1.48904

1.47645
1.47349
1.48372
invisible

1.47655
1.47350
1.48372
1.50861

DISPERSION.

D-C 0.00317
C-F 0.01054

0.00296
0.01023

0.00305
0.01022

WATER OF CRYSTALLIZATION OF CALCIUM SALT.

3 molecules

1.3 molecules

1 molecule.

MELTING POINT.

6.5°-8°

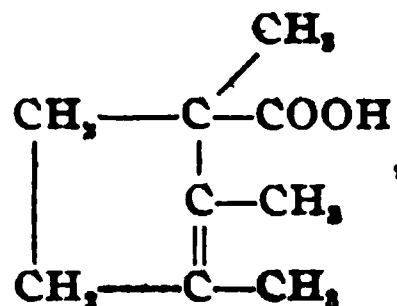
5°-8°

¹ Ber., 27, 3504.

² Ibid., 33, 3944.

³ Professor Eijkmann kindly called our attention to the fact that the pure lauronolic acid can be obtained in a crystalline form. In a private communication he states that he has obtained an acid melting at $+13^\circ$. Dr. Burke has very carefully repeated the preparation at the University of California but has not succeeded in obtaining an acid with a higher melting point than that given here. Professor Eijkmann's values for the index of refraction also differ slightly from ours.

Although both bromocamphoric anhydride and camphanic acid retain the gem dimethyl group, Lapworth and Lenton¹ have suggested for lauronolic acid the structure



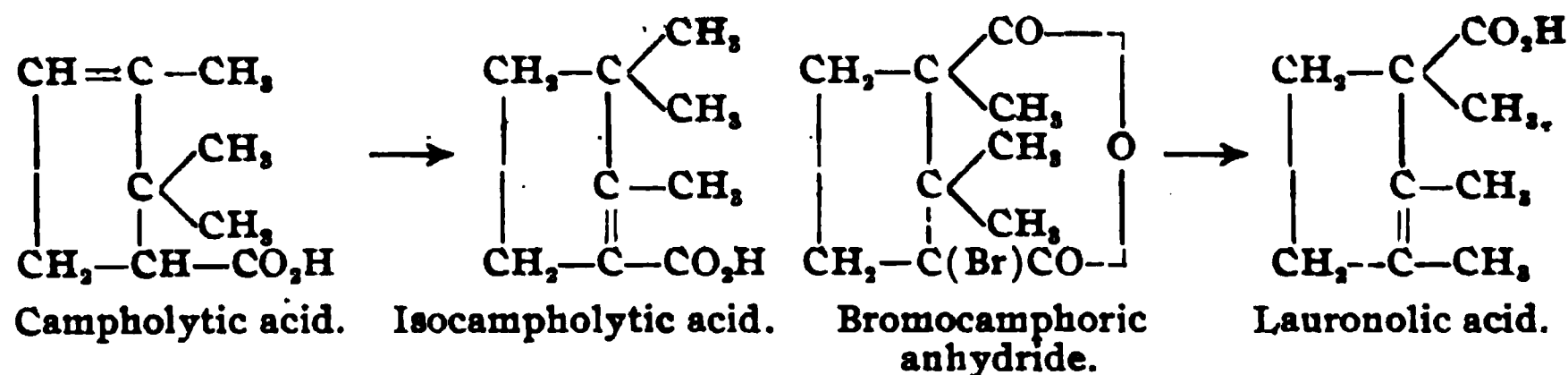
in which one methyl group has wandered, giving a 1,2,3-trimethyl compound, as being more in accord with the oxidation products obtained by Tiemann.² This structure has also been suggested by Eijkmann³ from a study of the optical properties of the acid, and is substantiated by the experimental part of this paper.

By distilling a mixture of the calcium salt of lauronolic acid and soda lime an almost quantitative yield of laurolene is obtained and this has been proven by synthesis⁴ to contain a 1,2,3-trimethyl group.

If the methyl group had not wandered, and the double bond were in the Δ^3 position, we would probably have an acid identical with the acid of Bredt⁵ and which on oxidation ought to give camphoronic acid. Oxidation of lauronolic acid, however, gives no trace of camphoronic acid.

The dissociation constant of lauronolic acid is 1.36×10^{-5} . That of α -campholytic acid is 1.0×10^{-5} . Although the difference is not very great, the lauronolic acid gives a distinctly higher value for K , which is difficult to explain, if the unsaturation is Δ^3 in each case. It has been shown⁶ that in both open chain and ring unsaturated acids a Δ^2 unsaturation invariably gives a greater dissociation constant than Δ^1 or Δ^3 . This would indicate that the double bond is Δ^2 .

The rearrangement which gives lauronolic acid is exactly parallel with the rearrangement of campholytic acid to isocampholytic ("isolauronolic") acid, as is apparent from the following formulas:



¹ *Brit. Assoc. Report*, 1900, 327. *J. Chem. Soc.*, 77, 1057; 79, 1289.

² *Ber.*, 33, 2944.

³ Private communication.

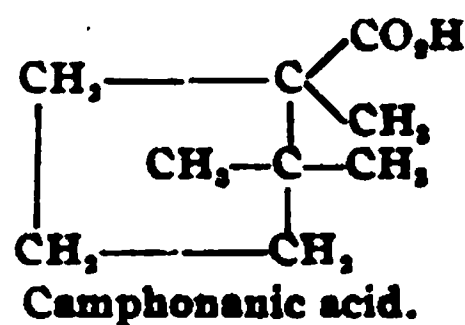
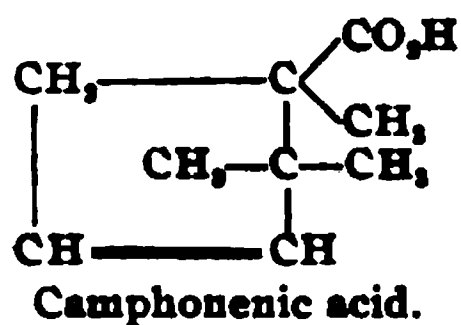
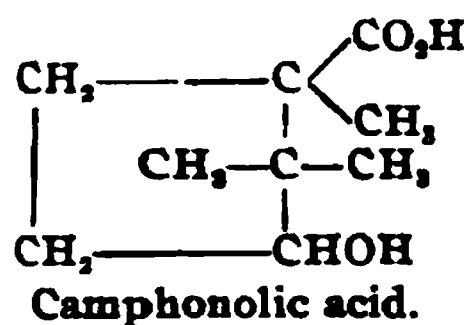
⁴ *THIS JOURNAL*, 32, 1064.

⁵ *Ber.*, 35, 1286.

⁶ Derick, *THIS JOURNAL*, 32, 1339.

In both cases a methyl group in the β -position with regard to carboxyl shifts to the γ -position.

We may now distinguish, clearly, three groups of unsaturated acids having the formula $C_8H_{13}COOH$. (1) Campholytic and isocampholytic acids, (2) the acid obtained by Bredt by the action of quinoline upon the bromine derivative of diphenyl camphorate. He has called this isolauronolic acid but as that name was formerly given to isocampholytic acid it seems best to drop it entirely from use, and in order to avoid confusion he now suggests¹ that this acid be called camphonenic acid, the three following acids being named as indicated. (3) The lauronolic acids



which have the methyl groups in the positions, 1,2,3. These are the only acids of this formula in the camphor series, for which the structure can at present be considered as fully established.

Experimental Part.

Bromocamphoric anhydride and Lauronolic Acid.—The bromocamphoric anhydride was prepared, and the decomposition into lauronolic acid and camphanic acid carried out according to the method of Aschan.² In every case after extraction with ether the last traces of ether were removed from the lauronolic acid by passing a current of hydrogen for from thirty to forty minutes, keeping the acid at a temperature of from 60–65° and under as low a pressure as could be obtained with a water pump, usually 30–35 mm.

If dried in a current of air or of carbon dioxide, the product soon decomposes and becomes black and tarry. With a current of hydrogen, however, we have found that the drying process may be continued indefinitely without any perceptible decomposition taking place.

One hundred grams of the anhydride yields nine to ten grams of yellowish colored acid. The crude acid gave a rotation $[\alpha]_D^{25} = +180^\circ$ to $+183^\circ$.

Purification of Lauronolic Acid.—Much difficulty has been experienced in obtaining a pure lauronolic acid, owing first to the ease with which the acid decomposed, second to the tendency on long standing at ordinary temperatures, or very quickly at even moderately high temperatures, to rearrange into the racemic form. The acid used in all of this work has been obtained by recovery from the purified calcium salt; the salt was decomposed with dilute hydrochloric acid and the pure lauronolic acid extracted with low-boiling ligroin and dried under diminished pressure

¹ Private communication.

² *Ber.*, 27, 3504.

with a current of hydrogen as described above. The acid thus obtained gave a constant rotation $[\alpha]_D^{25} = +187.7^\circ$.

An equally pure acid is obtained by distillation under diminished pressure with a Geryk pump, if a sufficiently low pressure can be obtained. At a pressure of $1/2$ to 1 mm. it distils constantly at 104° . A thermometer in the Wood's metal bath registered 113° – 115° . This acid gave approximately the same rotation as that obtained from the calcium salt.

Calcium Salt of Lauronolic Acid.—This salt, which was obtained by neutralizing the acid with milk of lime, is very difficultly soluble in water, and more soluble in cold than in hot, so that it can be recrystallized only by evaporating the solution. On evaporation a very pure salt separated on the surface of the solution in beautiful crystals. On analysis these were found to contain three molecules of water similar to the calcium salt of Fittig and Woringen.

0.2403 gram air-dried salt lost 0.0330 gram of H_2O at 110 – 115° and gave 0.0361 gram CaO .

0.2437 gram air-dried salt lost 0.0333 gram water at 115 – 118° and gave 0.0336 gram CaO .

0.2501 gram air-dried salt lost 0.0336 gram water at 110 – 115° and gave 0.0337 gram CaO .

Calculated for 3 mols. H_2O , 13.50.

Found: 13.73, 13.66, 13.43.

For the anhydrous salt, Ca , 11.56.

12.44, 11.40, 11.08, 11.60.

Bredt¹ states that he has obtained only two molecules of water of crystallization, but our results show that the acid undoubtedly contains three molecules. It loses a part of its water very readily at ordinary temperatures and, unless analyzed as soon as dry, gives results varying from one to three molecules. A sample of the salt which had been exposed to the air for two hours on a warm day gave only 6.70% H_2O .

Crystalline Lauronolic Acid.—Fittig and Woringen attempted to crystallize lauronolic acid but state that while it became very viscous in a freezing mixture it would not crystallize. In a private communication Professor Eijkmann stated that he had obtained the crystalline product and this led us to further attempts, which were successful.

The difficulty in getting the acid in crystalline form is, evidently, not on account of the low melting point of the substance, but rather on account of the tendency to supercool. When left for some time in a freezing mixture of hydrochloric acid and ice, at a temperature of -23° to -20° , it became very viscous but did not crystallize. With solid carbon dioxide and ether it forms a solid transparent mass, evidently simply the supercooled liquid, for on immersing in a freezing mixture at -20° it partly melts, then crystallizes into a solid, white mass.

By seeding the cooled acid the crystals were obtained in beautiful

¹ *J. prakt. Chem.*, 83, 395 (1911).

rosettes of long, concentric needles; the center of the rosette was slightly tinged with a green coloring matter, which seems to be characteristic of these compounds. The crystals melt at $+6.5^{\circ}$ to $+8^{\circ}$. (See above for Professor Eijkmann's results.)

Under atmospheric pressure the acid distils at $230-235^{\circ}$, but the vapor pressure at this temperature cannot be accurately determined, owing to the formation of various oxidation and decomposition products. At lower temperatures, however, the vapor pressure has been accurately determined by the method of Smith and Menzies,¹ using a bath of pure paraffin. At 184° , v. p. = 99–100 mm.

The specific gravity has been determined by means of a small specific gravity bulb at various temperatures.

$$D_4^{27.5} = 1.0109; D_4^{25} = 1.0133; D_4^{10} = 1.0249.$$

The rotation of the pure acid varies greatly with the temperature; the following specific rotations have been observed with the same sample of a pure acid in a ten cm. tube.

Temp.	$[\alpha]_D$	Temp.	$[\alpha]_D$	Temp.	$[\alpha]_D$
28°	187.1	21°	188.9	10°	194.1
25°	187.7	15°	191.1	6°	199.0
23°	188.2	11°	193.0		

Tiemann states that he has obtained a rotation of $+199^{\circ}$ at 19° ; we have not, however, been able to obtain as high a rotation at that temperature. The acid recovered from the purified calcium salt gives a constant rotation $[\alpha]_D^{25} = +187.7^{\circ}$.

The index of refraction determined for the sodium line D, and the three hydrogen lines C, F and G, gave the following results: D, 1.47586; C, 1.47269; F, 1.48323; G, 1.48904.

The electrical conductivity, determined with a saturated and a dilute solution, gave the dissociation constant $K = 1.36 \times 10^{-5}$.

Decomposition of Laurolonic Acid into Laurolene and Carbon Dioxide.—Blanc² obtained isolaurolene from α -campholytic acid by heating in a sealed tube at a temperature of 340° . Since at such high temperatures molecular rearrangements readily occur, this method would have no value from the standpoint of structure. We have endeavored to effect the same decomposition by keeping the acid at the boiling point. After 1–1½ hours the acid became very dark and somewhat viscous, owing probably to the formation of oxidation products, but no hydrocarbon was formed. On distilling, all but a little resinous material came over at 200° – 230° . A considerable portion of the distilled product was insoluble in sodium carbonate. On extracting with ether and distilling off the ether this product was obtained in crystalline form, melting at

¹ THIS JOURNAL, 33, 897.

² Bull. soc. chim., 19, 703.

49°–50°, showing that a part of the acid had rearranged into the isomeric lactone.

To another portion of the pure acid a little zinc chloride was added before distilling. The larger part of the product distilled now at 120°–125° and on redistilling came over constantly at 120°–121°. This was evidently the hydrocarbon laurone. It gave the following rotation, $[\alpha]_D^{30} = -5.36$.

The hydrocarbon was also obtained by mixing the calcium salt with soda lime and distilling. The distillate was again distilled with water vapor and the hydrocarbon separated from the first few cubic centimeters of the aqueous distillate. The boiling point at atmospheric pressure was 120°–122°.

Amide of Lauronic Acid.—To a small portion of the acid, cooled in ice water, one molecule of phosphorus pentachloride was added. The reaction was immediate and somewhat vigorous. After completion the product was poured into ice water to decompose the oxychlorides, and the chloride of the acid extracted with a little low-boiling ligroin. Concentrated ammonium hydroxide was added to this ligroin solution and the product allowed to stand until it no longer smelled of ammonia. It was then extracted with ether, the ethereal solution dried over sodium sulfate, and the ether distilled off. A dark, oily mass remained, which crystallized after standing for some time. On recrystallizing from water a very pure white, crystalline product was obtained, which melted at 72°. Three and a half grams of the acid yielded a little over one gram of the amide. This was evidently identical with the amide of Aschan.¹ In a ligroin solution (0.01 g. in 1 cc.) the amide gave the rotation, $[\alpha]_D^{25} = +94.61$.

A nitrogen determination gave 8.96% N; calculated for $C_{12}H_{23}CONH_2$, 9.15%.

An attempt was made to saponify the amide; 0.5 gram was heated on a steam bath with 1.5 molecules of sodium hydroxide, 10% solution, for four hours. On acidifying and extracting with ether the unchanged amide was recovered.

Dihydrolauronic Acid.—Fittig and Woringner have prepared the hydrobromide of lauronic acid and describe it as a very unstable product which readily decomposes, giving the unsaturated acid and campholactone.

We have prepared the hydriodide by passing hydriodic acid gas through a ligroin solution of lauronic acid. Twelve grams of lauronic acid in solution in low-boiling ligroin were placed in a U tube, and a slow stream of hydriodic acid passed in as long as it continued to be absorbed, usually 1½ to 2 hours. The solution was then placed in a distilling bulb, and a current of air passed through at ordinary temperatures until

¹ Beilstein, *Handbuch der organischen Chemie*, [1] 708.

the ligroin was completely evaporated. The iodide thus obtained in the form of yellow plates was evidently very unstable, since on standing it continued to evolve hydriodic acid.

Various methods of reducing the iodide thus formed have been employed with varying results.* The zinc-copper couple, magnesium and alcohol, zinc dust and water and zinc and hydriodic acid gave very poor results. The method which gave the best results, and the one finally adopted was zinc and absolute alcohol. To the crystals of the iodide as obtained above some zinc dust and absolute alcohol were added. There was very little evolution of gas and the product immediately passed into solution. After standing for a short time a few cubic centimeters of a solution of hydriodic acid were added and more hydriodic acid was passed through in order that any lauronolic acid which had been regenerated during the process might be again changed to the hydroiodide. Finally some hydrochloric acid was added and a somewhat vigorous evolution of hydrogen maintained for some time. After diluting with water the dihydro acid was extracted with ether and the recovered acid treated with sodium carbonate to remove a small amount of lactone which formed. Any remaining unsaturated acid was oxidized in the alkaline solution with potassium permanganate and the dihydro acid separated from the oxidation products by steam distillation.

Twelve grams of the unsaturated acid gave about three grams of the dihydro compound. Analysis:

Calculated for $C_8H_{14}CO_2H$: C, 69.23; H, 10.25.

Found: C, 69.03; H, 10.24.

Titration: 0.0588 gram acid required 3.85 cc. of 0.1 N NaOH for neutralization; calculated, 3.83 cc.

The following physical properties have been observed: $D_4^{23.5} = 0.9008$; $[\alpha]_D^{25.5} = +1.74^\circ$; v. p. at $178^\circ = 100$ mm.; v. p. at $215^\circ = 749$ mm. Index of refraction: $D = 1.45786$; $C = 1.45459$; $F = 1.46588$; $G = 1.47451$. Dispersion: $D-C = 0.00327$; $G-C = 0.01993$.

The Amide of Dihydrolauronolic Acid was prepared in the same way as the amide of lauronolic acid. It is exceedingly soluble in ether and has not been obtained in sufficient quantity to recrystallize. The crude product, washed with ether and dried on a porcelain plate, melted at $50^\circ-51^\circ$.

Inactive Lauronolic Acid.—The starting point of this preparation was artificial camphor obtained from the Ampere Electrochemical Co. of New York. The camphoric acid and bromocamphoric anhydride were prepared in the same way as the active compounds described above. The bromocamphoric acid anhydride melted at 214° . Mixed with the active anhydride it melted indefinitely but at about the same temperature.

On decomposing with sodium carbonate, inactive lauronolic acid and inactive camphanic acid were obtained. The inactive camphanic acid melted at $199^\circ-200^\circ$. The lauronolic acid thus obtained, like the active

variety, decomposed when distilled under ordinary conditions; it was purified by means of the calcium salt and also by distilling under diminished pressure. The calcium salt of the inactive acid crystallizes with one molecule of water of crystallization.

0.1385 gram air-dried salt lost 0.0070 gram H_2O and gave 0.0211 gram CaO .

0.1134 gram air-dried salt lost 0.0058 gram H_2O and gave 0.0174 gram CaO .

Calculated: For one mol. H_2O , 4.95; Ca (for anhydrous salt), 11.56. Found: I, 5.05, 11.40; II, 5.20, 11.52.

On cooling, the acid acts in the same way as the active variety; on standing in a freezing mixture at -20° for some time the acid becomes very viscous but does not solidify. With solid carbon dioxide and ether it forms a transparent solid, which in a mixture of ice and hydrochloric acid partly melts and then crystallizes. The crystals melt at $+5-8.5^\circ$. Vapor pressure at $192^\circ = 100$ mm. Specific gravity $D_4^{25} = 1.0318$. Index of refraction: $D = 1.47655$; $C = 1.47350$; $F = 1.48372$; $G = 1.50861$.

Campholactone.—As stated above, lauronolic acid readily rearranges under certain conditions into the isomeric lactone. Much difficulty has been experienced, however, in getting the lactone in crystalline form in sufficient quantities for study.

If lauronolic acid is heated with dilute mineral acid it chars and very little is obtained from the product. Fairly good yields have been obtained, however, by allowing the acid to stand for 12–24 hours with dilute hydrochloric acid (sp. gr. 1.1) at a temperature of $40^\circ-50^\circ$. The unchanged acid and lactone were distilled with water vapor, the distillate made alkaline with sodium carbonate, and the lactone extracted with ether. It is quite soluble in ligroin but by cooling in a freezing mixture may be readily recrystallized from it. The pure product melts at 50° . Rotation, $[\alpha]_D^{22} = -21.7^\circ$ (0.01 g. in 1 cc. of alcohol).

The lactone has been obtained in various ways from acids having widely differing rotations, but neither the method of preparation nor the rotation of the acid from which it is prepared has any influence upon the rotation of the lactone. The lactone from inactive lauronolic acid has not been prepared. That would, of course, be inactive.

Hydroxy Acid of Campholactone.—The lactone described above readily dissolves on warming with barium hydroxide, and the corresponding hydroxy acid is precipitated on acidifying. Fittig and Woringen state that they obtained the acid as an oil which crystallized on standing, but by first cooling in ice water both the solution of the salt and the hydrochloric acid, we obtained immediately, on acidifying, a beautiful crystalline precipitate of the hydroxy acid, m. p. 143° . (Tiemann gives $144^\circ-145^\circ$ after recrystallizing from water.)

In alcoholic solution (0.01 g. in 1 cc.) the acid gave the rotation $[\alpha]_D^{27} = +16.0^\circ$.

Synthesis of Acetolauroleone.—Sometime ago Blanc prepared acetoisolauroleone by Friedel and Crafts' reaction and from this effected a synthesis of isocampholytic acid. It seemed possible that we might synthesize lauronolic acid by a similar process from lauroleone. We have succeeded in obtaining acetolauroleone and its semicarbazone, but have not, as yet, succeeded in obtaining from this the lauronolic acid. The work will be continued and reported in detail later.

URBANA, ILL.

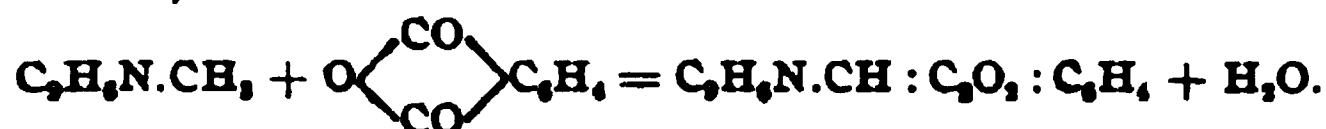
[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY,
No. 201.]

RESEARCHES ON QUINAZOLINES (TWENTY-EIGHTH PAPER). ON 4-QUINAZOLONE-2-PHTHALONES AND CERTAIN OF THEIR DERIVATIVES.¹

BY MARSTON TAYLOR BOBERT AND MICHAEL HEIDELBERGER.

Received December 25, 1911.

The well-known quinophthalones, or quinoline yellow dyes, are produced by condensing quinaldines with phthalic anhydride,² either by the action of heat alone or in the presence of such condensing agents as zinc chloride,



The product of this reaction is the alcohol-soluble quinoline yellow, or quinophthalone, which on sulfonation yields the water-soluble quinoline yellow S.

Two formulas naturally present themselves for quinophthalone,



In fact, two isomeric quinophthalones are known.

Through the skilful investigations of Eibner and his co-workers,³ it has been proven that the one ordinarily obtained (m. 235°) possesses formula I. To the isomer (m. 186°) is therefore assigned formula II. The two compounds appear to be formed in the reaction by two distinct series of changes,⁴ and neither substance is to be regarded as an inter-

¹ Read at the Washington Meeting of the Society, December 28, 1911.

² Jacobsen and Reimer, D. R. P. No. 23188 (1882) and *Ber.*, 16, 513, 1082, 1892, 2602 (1883). Traub, *Ber.*, 16, 297, 878 (1883). Geigy and Königs, *Ibid.*, 18, 2407 (1885). Königs and Nef, *Ibid.*, 19, 2428 (1886). Panajotow, *Ibid.*, 28, 1511 (1895); D. R. P. Nos. 23188 and 25144. Friedländer, 1, 161, 162, *et al.*

³ *Ann.*, 315, 303 (1901). *Ber.*, 34, 2303 (1901); 35, 1656, 2297 (1902); 36, 1860 (1903); 37, 3006, 3011, 3018, 3023, 3605 (1904); 38, 3353 (1905); 39, 2202, 2215, 2245 (1906). *Chem. Ztg.*, 28, 1206 (1904). *Chem. Zentralbl.*, 1905, I, 910.

⁴ Eibner, *Ber.*, 37, 3605 (1904); *Chem. Ztg.*, 28, 1206 (1904).

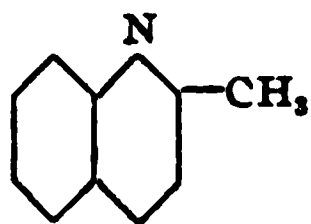
mediate product in the formation of the other. These parallel series of reactions lead, in the one case, to the formation of an alkine addition product which then passes into the unsymmetrical phthalone by loss of water; in the other case, to a quinolyacetophenone-*o*-carbonic acid which yields the symmetrical phthalone by loss of water. Both phthalones give with sodium ethylate the same red sodium salt, which with dilute acid yields the symmetrical phthalone (m. 235°). This conversion of the unsymmetrical into the symmetrical phthalone is entirely analogous to that of benzalphthalide into β -phenylindandione.¹

In addition to the quinophthalones, phthalones have been obtained also in the pyridine,² benzimidazole,³ phthalazine,⁴ ethenylaminophenylmercaptan,⁵ nitromethane⁶ and possibly other series, but so far as we are aware none have been described as yet from the quinazoline series.

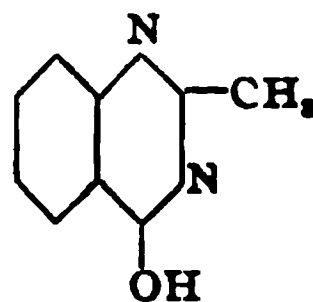
Other anhydrides, such as succinic⁷ and naphthalic,⁸ have been employed in lieu of phthalic, and the free acids can often be used instead of their anhydrides.

Using the imides in place of the anhydrides, analogously constituted phthalines⁹ are obtained.

In the present article are described certain phthalones belonging to the quinazoline series. The 2-methyl-4-quinazolone (2-methyl-4-hydroxyquinazoline) compounds were chosen for these experiments, since they can be readily and rapidly prepared pure and in any desired amount,¹⁰ and are of quinaldine type:



Quinaldine.



2-Methyl-4-hydroxyquinazoline.

2-Methyl-4-quinazolone condenses smoothly with phthalic anhydride to the symmetrical phthalone, which behaves as a weak acid, forming

¹ Nathanson, *Ber.*, 26, 2576 (1893).

² Jacobsen and Reimer, *Ber.*, 16, 2602 (1883). von Huber, *Ibid.*, 36, 1653 (1903). Gaebelé, *Ibid.*, 36, 3913 (1903). Scholze, *Ibid.*, 38, 2806 (1905).

³ Bamberger and Wulz, *Ber.*, 24, 2053 (1891). Bamberger and Berlé, *Ibid.*, 25, 274 (1892); *Ann.*, 273, 315 (1893).

⁴ Gabriel and Eschenbach, *Ber.*, 30, 3034 (1897).

⁵ P. Jacobson, *Ibid.*, 21, 2624 (1888).

⁶ Gabriel, *Ibid.*, 36, 570 (1903).

⁷ Eibner and Lange, *Ann.*, 315, 303 (1901).

⁸ Eibner and Löbering, *Ber.*, 39, 2215 (1906).

⁹ Jacobsen and Reimer, *Ibid.*, 16, 2608 (1883). Eibner and Lange, *Ann.*, 315, 328 (1901). Eibner and Hofmann, *Ber.*, 37, 3018 (1904).

¹⁰ Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902). Bogert, *et al.*, *THIS JOURNAL*, 25, 788 (1910).

a yellow mono-sodium salt and a red di-sodium salt, as well as a red mon-anil, a mono-phenylhydrazone and a sulfonic acid. Energetic reduction converts the phthalone into the corresponding hydrindone. The sulfonic acid of the phthalone when brominated in aqueous solution yields a dibrom 2-methyl-4-quinazolone, which is not the 6,8-dibrom compound,¹ a pentabrom 2-methyl-4-quinazolone, a monobrom 2-methyl-4-quinazolone sulfonic acid, phthalic and sulfuric acids.² An interesting feature of the reaction is that the bromine splits off the phthalic acid from the quinazolone nucleus.

6-Nitro and 7-acetamino 2-methyl-4-quinazolone condense similarly to phthalones.

With phthalimide, 2-methyl-4-quinazolone condenses to the unsymmetrical or β -phthaline, with formation of a small amount of what appears to be a bis-quinazolone phthaline.

2-Methyl-4-quinazolone and succinic anhydride react vigorously with production of a tarry mass, from which a colorless anhydro body may be isolated.

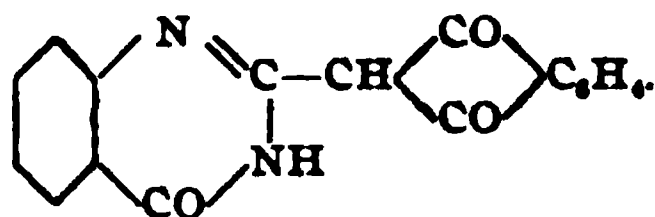
2-Methyl-4-quinazolones carrying alkyl groups in position 3 either refuse to condense with phthalic anhydride or give only a small yield of the phthalone.

In none of the experiments was the formation of any unsymmetrical phthalone observed, nor could we isolate any intermediate product except the phthalate of the quinazolone.

Like the quinophthalones, these phthalones act as yellow dyestuffs, but in tinctorial power they seem inferior to the former.

Experimental.

4 - Quinazolone - 2 - phthalone-(4 - hydroxyquinazoline - 2 - phthalone, 2 - indandionyl - 4 - quinazolone, β - (4'-quinazolonyl-2') - diketohydrindene),³



—An intimate mixture of equimolecular amounts of 2-methyl-4-quinazolone and phthalic anhydride was heated rapidly to about 200°. At about 160° the mixture fused to a homogeneous, yellowish brown liquid. Evolution of water began above this point, gradually becoming more rapid as the temperature rose, and finally causing the melt to boil vigorously, the color of the mixture darkening to a deep red and yellow needles separating. The mass soon solidified at this temperature (200°), but

¹ Bogert and Hand, THIS JOURNAL, 25, 935 (1903).

² Compare Limpricht, *Ann.*, 181, 193 (1876). Kelbe, *Ibid.*, 210, 37, 48 (1881).

³ For the sake of brevity, these compounds will be generally designated quinazolone phthalones and formulated accordingly.

the heating was continued for about three hours to complete the reaction. The crystalline brownish yellow cake thus obtained was pulverized and extracted repeatedly with small amounts of boiling 95% alcohol, to remove unchanged initial materials and certain brown by-products (see beyond). The yellow residue was then rubbed up thoroughly to a paste with sodium ethylate solution, giving at once the bright orange-red di-sodium salt. The mixture was thinned with absolute alcohol and heated for half an hour on the water-bath, to insure complete conversion to the di-sodium salt and the consequent transformation of any unsymmetrical phthalone to the symmetrical form. When cold, the mixture was filtered and the di-sodium salt rubbed up with hot water, causing immediate hydrolysis to the orange-yellow, difficultly soluble mono-sodium salt. Acidification of this with acetic acid liberated the pale yellow flocculent phthalone itself, which was filtered off, washed with hot, dilute acetic acid, then with hot water, and thoroughly dried. Average yield, 70%. As thus prepared, it was quite pure and tribo-electric. For analysis, it was again crystallized from glacial acetic acid, and then lost its tribo-electric properties:

Found: C, 70.04; H, 3.63; N, 9.88. Calculated for $C_{17}H_{10}O_2N_2$: C, 70.32; H, 3.47; N, 9.66.

Instead of the method of purification just given, the crude phthalone may be washed thoroughly with boiling dilute hydrochloric acid, then with water, and recrystallized from glacial acetic acid; or, it may be dissolved in warm, concentrated sulfuric acid, reprecipitated by dilution, and the precipitate crystallized until pure.

The pure phthalone separates from glacial acetic acid either in pale yellow prismatic needles, often united in sheaves, or in hexagonal plates. The two forms melt at the same point, and no change in melting-point occurs on mixing the two. By dissolving the plates in hot chloroform, precipitating with alcohol or ether, and recrystallizing from glacial acetic acid, the needles are obtained. It is of interest in this connection to note that pyrophthalone is also dimorphous,¹ crystallizing in both needles and leaflets, the latter being the more stable form.

Heated above 200°, the phthalone sublimes unchanged in wooly masses of pale yellow minute needles, melting at about 318° (cor.). It is very easily soluble in hot phenylhydrazine; soluble in chloroform, hot glacial acetic acid, aniline or pyridine; difficultly soluble in alcohol, acetone, amyl acetate or benzene; and practically insoluble in water or ether.

Presumably because of the $\text{—CO.NH—} \rightleftharpoons \text{—C(OH):N—}$ group of the quinazolone nucleus, in contradistinction to quinophthalone, it acts as a weak acid. Thus, while it is but slightly soluble in cold, dilute ammonium

¹ Eibner and Löbering, *Ber.*, 39, 2447 (1906). Löbering, *Inaug. Dissert., Techn. Hochsch. München*, 1907, p. 47.

hydroxide solution, it dissolves readily in it on warming. In boiling sodium hydroxide or sodium carbonate solutions, it dissolves with difficulty, since the mono-sodium salt is itself difficultly soluble in alkaline solutions. From these solutions it is precipitated by acetic acid. Concentrated alcoholic potassium hydroxide solution does not decompose it, but fusion with caustic alkali or distillation with calcium oxide does. The basic properties of the quinazolone are submerged by the phthalyl residue, so that the phthalone does not form a hydrochloride or chlorplatinate under any ordinary conditions. In fact the phthalone is not only insoluble in the boiling concentrated acid, but is also very resistant to its action even when heated with it under pressure. Seven hours' heating with the concentrated acid at $190-220^{\circ}$ left most of the phthalone unchanged; but seven hours' heating at 270° decomposed practically all of it, only phthalic acid being isolated from the blackened tube contents. In experiments at intermediate temperatures, both phthalic acid and 2-methyl-4-quinazolone were identified among the products. In concentrated sulfuric acid, it dissolves to an orange solution, from which it separates unchanged on dilution. Hot, fuming sulfuric acid sulfonates it, while dilute nitric acid is without action upon it.

The use of zinc chloride in condensing phthalic anhydride with the quinazolone is objectionable in that it leads to the formation of tarry products and renders purification more troublesome.

Sundry experiments were carried out with the object of isolating either the unsymmetrical phthalone or intermediate products in the condensation of the quinazolone and phthalic anhydride. An intimate mixture of the two was unchanged after four hours' heating at 100° . The mixture was then dissolved in toluene and boiled gently for 72 hours, but the only change observed was a slight yellowing of the solution.

2-Methyl-4-Quinazolone Phthalate, $C_9H_8ON_2 \cdot C_8H_4(COOH)_2$.—In one experiment, ten grams of the quinazolone were mixed with an excess (14 g.) of phthalic anhydride, this excess of anhydride being added as a flux on account of the high melting-point of the quinazolone (235°) and of the phthalone, and the mixture heated an hour and a half at $150-170^{\circ}$, giving a yellowish brown semifluid melt. On extraction with boiling water, the crude phthalone remained undissolved (yield, about 30%), while from the aqueous extract there separated on cooling beautiful light yellow fluorescent prismatic needles of the quinazolone phthalate, carrying a molecule of water of crystallization which was driven off at 110° :

Found: H_2O , 5.50. Calculated for $C_{17}H_{14}O_4N_2 \cdot H_2O : H_2O$, 5.24.

Analysis of the anhydrous material resulted as follows:

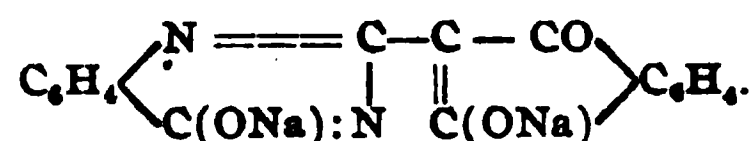
Found: C, 62.57, 62.43, 62.62; H, 4.35, 4.04, 4.38; N, 9.14, 9.03. Calculated for $C_{17}H_{14}O_4N_2$: C, 62.55; H, 4.33; N, 8.59.

Occasionally the salt crystallizes anhydrous in plates. If heated quickly to within a few degrees of its melting-point, the anhydrous salt melts at 171° (cor.) with evolution of gas. If heated above its m. p. water and phthalic anhydride are driven off and the phthalone formed, together with small amounts of decomposition products.

This phthalate is easily soluble in glacial acetic acid; soluble in alcohol, acetone, amyl acetate, nitrobenzene or hot water; difficultly soluble in chloroform; very slightly soluble in ether or hot benzene; and practically insoluble in carbon tetrachloride or ligroin. In aqueous sodium carbonate solution, it dissolves with effervescence. Its solution in aqueous potassium hydroxide solution on saturation with carbon dioxide precipitates 2-methyl-4-quinazolone. Its aqueous solution is not precipitated by silver nitrate or copper sulfate solutions. The substance is a weak dye, and in water solution dyes silk a pale greenish yellow. In concentrated sulfuric acid, it dissolves to a yellow solution which when heated to 100° and then diluted does not separate any phthalone. It seems odd that the phthalone should form a salt with phthalic and not with the strong mineral acids.

The brown alcohol-soluble by-products, formed in the condensation of the quinazolone and phthalic anhydride at 200° , were also investigated and two substances isolated: one crystalline, not melting below 313° (uncor.), the other amorphous, and melting to a tar in the neighborhood of $220-225^{\circ}$ (uncor.). Not enough of either substance was obtained for further study.

Di-Sodium Salt of 4-Quinazolone-2-Phthalone,



—The phthalone was boiled for several hours with excess of an absolute alcohol solution of sodium ethylate, protecting the reflux with a calcium chloride guard tube. The orange-red salt was filtered off, dried in a desiccator, pulverized fine and washed with absolute alcohol until the washings failed to show an alkaline reaction on dilution. It was washed finally with a little absolute ether, dried *in vacuo* and analyzed:

Found: Na, 13.49, 13.50. Calculated for $\text{C}_{17}\text{H}_8\text{O}_3\text{N}_2\text{Na}_2$: Na, 13.77.

The pure salt forms an orange-red, micro-crystalline powder, which is gradually hydrolyzed by the moisture of the air to the yellow mono-sodium salt. Boiling dilute sodium hydroxide effects a similar change, but boiling water hydrolyzes it completely to the phthalone. Acetic acid immediately liberates the phthalone.

Mono-Sodium Salt, $\text{C}_{17}\text{H}_8\text{O}_3\text{N}_2\text{Na}$.—The phthalone was boiled for several hours with dilute sodium hydroxide solution, to insure complete conversion to the difficultly soluble orange-yellow salt. On filtering the hot

solution, most of the salt remained on the filter, but some also separated from the filtrate on cooling. The two lots thus obtained were combined, dried at 110° , and exposed to the air, to convert any excess of caustic alkali to the carbonate (which is difficultly soluble in absolute alcohol). The crude salt was then extracted repeatedly with boiling absolute alcohol, and from these extracts the pure salt separated on cooling. It was washed with ether, pulverized, dried, and analyzed:

Found: Na, 7.31. Calculated for $C_{17}H_9O_2N_2Na$: Na, 7.37.

The salt as thus prepared is a pale yellowish microcrystalline solid, difficultly soluble in absolute alcohol. It is moderately soluble in water, but the aqueous solution on boiling precipitates the free phthalone. It acts as a weak dye, its aqueous solution dyeing silk a pale yellow.

Since the sodium salt of 2-methyl-4-quinazolone is colorless, while that of the quinophthalone is red, it seems most probable that the above mono-sodium salt carries the sodium in the quinazolone portion of the nucleus.

Silver Salt.—The phthalone was dissolved in dilute ammonium hydroxide solution, an ammoniacal solution of silver nitrate added, and the mixture boiled. On cooling, beautiful light yellow hair-like needles of the silver salt separated.



—Five grams of 4-quinazolone-2-phthalone were boiled for two hours and a half with a solution of 25 grams sodium hydroxide in 300 cc. of water, zinc dust being added in small portions from time to time. The solution slowly turned a dark green. As the solid material in the flask balled together somewhat and was protecting part of the phthalone from reduction, it was removed, rubbed up to a thin paste in a mortar, returned to the flask, the boiling with alkali and zinc dust continued for 12 hours longer, and the mixture then allowed to cool. The solid was filtered out and washed with hot water. Warming this material with dilute hydrochloric acid proved an unsatisfactory method of removing the excess of zinc, and we found it necessary to treat first with cold concentrated acid until vigorous effervescence ceased and then warm the solution until no more evolution of hydrogen occurred (several hours). The mixture was diluted with a large volume of water, boiled, allowed to cool, and the undissolved hydrindone filtered out and purified by repeated crystallization from alcohol. The yield was poor:

Found: C, 73.78; H, 4.65; N, 10.29. Calculated for $C_{17}H_{11}O_2N_2$: C, 73.88; H, 4.38; N, 10.15.

The hydrindone forms olive-yellow microscopic crystals, which sublime and turn orange above 160° , finally melting to a red liquid at about 328° (uncor.) with previous softening and decomposition. It is practically

insoluble in water or ether; very slightly soluble in hot chloroform, amyl acetate or toluene; and difficultly soluble in ethyl or amyl alcohol.

In this preparation, we did not encounter any intermediate product similar to the dihydrostilbazole-*o*-carbonic acid isolated by Gaebelé¹ in his preparation of the hydrindone from pyrophthalone.

4-Quinazolone-2-Phthalone Mon-anil, $\text{C}_8\text{H}_5\text{ON}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{N}\cdot\text{C}_6\text{H}_5$.—Eibner² has shown that some phthalones yield di-anils, while others give only mon-anils.

When 4-quinazolone-2-phthalone was dissolved in aniline and the solution boiled, no change occurred. But when such a solution was heated nearly to its boiling point and small amounts of anhydrous zinc chloride gradually added, an immediate and vigorous evolution of water ensued. For 5 g. of the phthalone, 3 g. zinc chloride were used. The reaction was completed by gently boiling the solution for an hour and a half, and then allowing it to cool. The pasty mass was filtered and the insoluble, bright yellow, crystalline residue washed with alcohol. Upon further addition of alcohol to the filtrate, more of the yellow solid precipitated and was added to the first lot. This yellow solid was pulverized fine, washed thoroughly with alcohol, and then with boiling, dilute ammonium hydroxide solution (to remove unchanged phthalone). From these ammoniacal extracts, on cooling, a colorless zinc salt separated. The yellow solid, as thus purified, proved to be a double zinc chloride itself, as described beyond, and gave qualitative tests for both zinc and halogen. It was decomposed by dissolving it in boiling glacial acetic acid, adding water to turbidity, then acid until clear, boiling the orange-red solution 10 or 20 minutes and cooling.³ Minute scarlet needles separated. These were dried, extracted with boiling carbon tetrachloride, and the residue crystallized two or three times from strong acetic acid. As thus obtained, it showed only a faint trace of ash, and was analyzed with the following results:

Found: C, 75.54; H, 4.15; N, 11.99, 11.86. Calculated for $\text{C}_{22}\text{H}_{15}\text{O}_2\text{N}_2$: C, 75.59; H, 4.14; N, 11.51.

The anil crystallizes from alcohol in brilliant scarlet needles, melting at 284–5° (uncor.), with previous sublimation and sintering. It is strongly tribo-electric. In chloroform, pyridine, phenylhydrazine, or hot strong acetic acid, it is readily soluble; moderately soluble in acetone or benzene; difficultly soluble in methyl or ethyl alcohol, ether or carbon tetrachloride; practically insoluble in water or aqueous ammonium hydroxide solution. It is quite stable to mineral acids, but boiling 1 : 1 hydrochloric acid

¹ *Loc. cit.*

² *Ber.*, 37, 3605 (1904). *Chem. Ztg.*, 28, 1206 (1904).

³ Some hydrolysis of the anil often results from this boiling with strong acetic acid.

gradually hydrolyzes it to the phthalone and aniline again. Boiled for a few minutes with dilute caustic alkali solution, a light yellow alkali salt is formed, from which acetic acid liberates the red anil.

Sodium Salt.—The anil was boiled for a few minutes with excess of dilute sodium hydroxide solution. The light yellow salt was filtered off and washed thoroughly with absolute alcohol until all free alkali was removed. Some of the salt is lost by this treatment. The purified salt was dried at 110° and analyzed:

Found: Na, 5.99. Calculated for $C_{22}H_{14}O_2N_2Na$: Na, 5.94.

In presence of moisture, this yellow sodium salt rapidly hydrolyzes to the red anil. Its color is not changed by treatment with a solution of sodium ethylate in absolute alcohol.

Double Salt of Zinc Chloride and the Anil.—A portion of the crude, yellow, double zinc salt isolated as an intermediate product in the preparation of the anil was dissolved in chloroform, the solution concentrated and the salt re-precipitated by the addition of hot alcohol. The bright yellow, microcrystalline precipitate obtained on cooling was further purified by a repetition of this treatment, dried at $120-30^{\circ}$ and analyzed:

Found: N, 9.97. Calculated for $2C_{22}H_{14}O_2N_2 \cdot ZnCl_2$: N, 9.70.

A hot alcoholic solution of the anil treated with a similar solution of zinc chloride slowly deposited on cooling a bright yellow crystalline double zinc salt apparently identical with the above.

Another Anil of the Phthalone.—In the final purification of the anil described above, the crude product was extracted with boiling carbon tetrachloride. In one case only, this orange extract, on concentration to small volume and cooling, deposited minute red crystals, melting at 258° (uncor.), with previous sublimation. Under the microscope, these crystals appeared homogeneous and on analysis gave the following figure:

Found: N, 10.91. Calculated for $(C_{17}H_8O_2N_2)_2 \cdot N \cdot C_6H_5$: N, 10.99.

This corresponds to a condensation of one molecule of aniline with two of the phthalone. The amount obtained was insufficient for further investigation, and we did not encounter it in subsequent preparations of the anil.

4 - Quinazolone - 2 - Phthalone Monophenylhydrazone, $C_{22}H_{14}ON_2$.

$CH.CO.C_6H_4.C : N.NHC_6H_5$.—Eibner and Hofmann¹ were unable to prepare the phenylhydrazone of quinophthalone by the direct action of phenylhydrazine upon the phthalone, but succeeded in obtaining it by the action of the hydrazine upon the anil, a reaction due to von Walther.²

Efforts to secure the phenylhydrazone of the quinazolone phthalone in similar fashion, from the anil, proved unsuccessful. We therefore

¹ Ber., 37, 3018 (1904).

² J. prakt. Chem., [2] 53, 455 (1896).

heated the phthalone itself with excess of phenylhydrazine for 20 minutes over the flame. Water was given off, and the color of the solution became dark red. When cold, ether was added to the viscous mass, the orange-red precipitate filtered off, washed well with ether, and then boiled with dilute ammonium hydroxide solution to remove any unchanged phthalone. The residue crystallized twice from alcohol gave an orange-brown, micro-crystalline powder, melting at about 225° (uncor.) with evolution of gas. The yield was poor and not enough of the material was obtained for further purification:

Found: N, 15.00. Calculated for $C_{22}H_{16}O_2N_4$: N, 14.74.

The compound is insoluble in water, and difficultly soluble in alcohol or amyl acetate.

An attempt to prepare the oxime of 4-quinazalone-2-phthalone by boiling the phthalone with excess of hydroxylamine hydrochloride and dilute sodium carbonate resulted merely in the immediate formation of the difficultly soluble, bright yellow mono-sodium salt of the phthalone. Eibner was likewise unsuccessful in his efforts to isolate oximes of quino-phthalones.

A similar lack of success attended our efforts to prepare the semicarbazone of the phthalone. On boiling for three hours a glacial acetic acid solution of the phthalone, semicarbazide hydrochloride and fused sodium acetate, no change could be detected, even after adding a little acetic anhydride. Two grams anhydrous zinc chloride were then added and the boiling continued for four hours. On cooling the bright yellow, double zinc chloride salt of the phthalone, already described, and unchanged phthalone separated. No semicarbazone could be isolated.

4-Quinazalone-2-Phthalone-6-Sulfonic Acid, $HO_3S.C_6H_4ON_2.CH:C_2O_2:C_6H_4$. —The phthalone was dissolved in a mixture of one part concentrated to about three parts Nordhausen fuming sulfuric acid and the solution heated at 100° until a test portion dissolved completely in water (about three hours). The deep red acid solution when cold was poured upon cracked ice and most of the sulfo acid separated as a bright yellow amorphous solid. It was filtered out, and the filtrate used for the preparation of the di-sodium salt described beyond. The crude sulfo acid was boiled with a large volume of water, filtered, and the filtrate concentrated to incipient crystallization. On cooling, minute orange-yellow, glistening scales, of greasy feel, were deposited. Yield, 9 g. from 10 g. phthalone. It was recrystallized from strong (not glacial) acetic acid, dried thoroughly at 120° , and analyzed by fusion in a silver crucible with sodium hydroxide and nitrate, leaching the melt with water, and weighing as barium sulfate:

Found: S, 8.75. Calculated for $C_{17}H_{10}O_6N_2S$: S, 8.66.

The anhydrous acid is pale yellow and dimorphous, crystallizing either in microscopic, lenticular plates or in aggregates of minute needles. The

latter is the unstable form and soon changes into the plate form. On heating, the substance gradually darkens, sinters, and finally melts to a black liquid in the vicinity of $355-60^{\circ}$ (uncor.). It absorbs moisture eagerly from the air and turns orange. It is easily soluble in hot water, but not readily in cold; very difficultly soluble in glacial acetic acid, but dissolves quite easily in the hot acid upon the addition of a small amount of water. Fusion with caustic alkali breaks it down. With concentrated nitric acid at 100° , simple nitration seems to take place, but this reaction was not followed farther. Heated for seven hours at 200° with concentrated hydrochloric acid, it is easily and cleanly split into phthalic acid and what is evidently a 2-methyl-4-quinazolone sulfonic acid. The sulfo group is therefore on the quinazolone part of the molecule, most probably at position 6.

Mono-Sodium Salt, $C_{17}H_9O_8N_2 \cdot SO_3Na$.—The free acid was dissolved in hot water, the calculated amount of sodium hydroxide added, and the solution concentrated. On cooling, the salt separated in light yellow plates, which were recrystallized from water, washed with alcohol and ether, dried to constant weight and analyzed:

Found: Na, 5.87. Calculated for $C_{17}H_9O_8N_2SNa$: Na, 5.86.

On adding sodium hydroxide to an aqueous solution of the salt, the formation of the di-sodium salt is indicated by the change in the color of the solution from a light to a dark yellow.



—The filtrate from the original precipitate of crude sulfonic acid still retained considerable of this acid. It was therefore neutralized with excess of barium hydroxide solution, or barium carbonate, and the mass boiled with slight excess of sodium carbonate solution and filtered. The filtrate was concentrated, filtered from a further separation of barium salts, and evaporated to small volume. On cooling, the disodium salt separated as an orange-yellow crystalline solid, carrying water of crystallization. It was dried to constant weight and analyzed:

Found: Na, 11.01. Calculated for $C_{17}H_9O_8N_2SNa_2$: Na, 11.11.

The determination of the water of crystallization gave the following results:

Found: H_2O , 14.42, 13.98. Calculated for $C_{17}H_9O_8N_2SNa_2 \cdot 4H_2O$: H_2O , 14.82.

Although this result is not very satisfactory, it appears to indicate the presence of four molecules of water of crystallization.

The presence of the sulfo group materially increases the acidity of the quinazoline portion of the molecule, and it should follow that the above di-sodium salt would carry one atom of sodium in the sulfo group and the other in the quinazoline hydroxyl, and this deduction is in agreement

with the behavior of the compound. The strengthening influence of the sulfo group is evidenced also by the fact that aqueous solutions of this di-sodium salt are unchanged by boiling, whereas the corresponding mono-sodium salt of the unsulfonated phthalone is quickly hydrolyzed by such treatment.

Its aqueous solutions dye wool or silk light yellow shades. As this salt corresponds to the technical quinoline yellow S, it might be called quinazolone yellow S.

In the analysis of the sulfo acid by fusion with sodium hydroxide a brilliant red developed before the decomposition of the substance. We think that this may have been due to the formation of the tri-sodium salt, but an attempt to obtain such a red salt by the action of sodium ethylate upon the di-sodium salt was unsuccessful.

Barium Salt, $(C_{17}H_9O_3N_2SO_3)_2Ba$.—A hot, aqueous solution of the free acid was precipitated with slightly more than the calculated amount of barium hydroxide solution, the precipitate filtered out, washed with cold water, recrystallized from boiling water, dried to constant weight and analyzed:

Found: Ba, 15.61. Calculated for $(C_{17}H_9O_3N_2S)_2Ba$: Ba, 15.46.

Minute, glistening pale yellow crystals, which are tribo-electric. It is difficultly soluble in cold water, moderately soluble in hot.

Bromination of 4-Quinazolone-2-Phthalone Sulfonic Acid.—By the action of bromine upon the aqueous solution of the sulfo acid, there were formed a di- and a penta-bromo-2-methyl-4-quinazolone, a mono-bromo-2-methyl-4-quinazolone sulfonic acid, phthalic acid and sulfuric acid.

The sulfo acid was dissolved in hot water and bromine added very cautiously until present in excess. The reaction was quite vigorous and towards its close a colorless crystalline precipitate separated which increased as the solution cooled. The mixture was allowed to stand for an hour or two and then, without removing the precipitate, boiled until the excess of bromine was driven off. A colorless solution resulted, showing that all the original phthalone sulfonic acid had been decomposed. When the mixture cooled, the precipitate was filtered out and the filtrate used for the separation of the other products of the reaction as described beyond.

Dibromo-2-Methyl-4-Quinazolone, $C_9H_6ON_2Br_2$, was isolated from the above precipitate by extraction with boiling water, and the residue used for the recovery of the pentabrom compound which follows. On cooling, there separated from these aqueous extracts arborescent masses of colorless, delicate needles. These were recrystallized from water, dried at 110° and analyzed, after a qualitative test had shown the absence of sulfur:

Found: N, 8.82; Br, 49.64. Calculated for $C_9H_6ON_2Br_2$: N, 8.81; Br, 50.28.

When heated, the compound gradually darkens and melts at about 293° (uncor.) with decomposition. It is difficultly soluble in hot water, more readily in hot alcohol or hot benzene. It is soluble also in hot, dilute potassium hydroxide solution and is reprecipitated from this solution by saturation with carbon dioxide. A comparison with the 6,8-dibromo-2-methyl-4-quinazolone of Bogert and Hand¹ shows that the two are not identical.

Pentabromo-2-Methyl-4-Quinazolone, $C_8H_5ON_2Br_5$.—After the extraction of the foregoing dibrom compound with boiling water, as described, the undissolved residue was crystallized from dilute alcohol and colorless prismatic needles of the pentabrom compound obtained:

Found: N, 5.63; Br, 72.02. Calculated for $C_8H_5ON_2Br_5$: N, 5.05; Br, 72.05.

This quinazolone melts with decomposition at about 243.5° (uncor.). It is easily soluble in glacial acetic acid or in hot alcohol; moderately soluble in chloroform, acetone, benzene or cold alcohol; difficultly soluble in ether; and practically insoluble in water. In hot, dilute potassium hydroxide solution it dissolves, and can be reprecipitated by saturating the solution with carbon dioxide.

Monobrom-2-Methyl-4-Quinazolone Monosulfonic Acid.—The filtrate from the original precipitate of crude bromquinazolones was concentrated somewhat, and to the boiling solution barium hydroxide solution was added in moderate excess and the boiling continued for 15 minutes. The heavy precipitate of barium sulfate showed that the sulfo group had been split off, at least in part, from the phthalone sulfonic acid by the bromine, and accounted for the sulfur-free quinazolones described above. The barium sulfate was filtered out and the filtrate on evaporation deposited beautiful colorless needles of the *barium salt*, contaminated with a few warty aggregates of barium phthalate which latter were readily picked out. The residual colorless needles when recrystallized from water carry from four to five molecules of water of crystallization:

Found: H_2O , 7.71. Calculated for $(C_8H_5O_4N_2BrS)_2Ba \cdot 4\frac{1}{2}H_2O$: H_2O , 7.38.

All but one molecule of this water can be driven off by drying at 110° to constant weight. The salt thus dried was analyzed by dissolving it in water, precipitating the barium with a very slight excess of sulfuric acid, and washing the precipitate thoroughly with hot water:

Found: Ba, 17.38. Calculated for $(C_8H_5O_4N_2BrS)_2Ba \cdot H_2O$: Ba, 17.36.

This salt carrying one molecule of water is very hygroscopic.

The *free acid* was recovered from the filtrate and washings of the barium sulfate precipitate in the analysis of the barium salt. These were combined; evaporated to dryness, the amorphous residue taken up with a little hot absolute methyl alcohol, the solution reprecipitated with ether, the precipitate dissolved in absolute ethyl alcohol, filtered, the filtrate

¹ THIS JOURNAL, 25, 935 (1903).

reprecipitated with ether, and this solution in alcohol and reprecipitation with ether repeated once more. The acid was thus obtained as a grayish amorphous solid. Like its barium salt, it retains one molecule of water of crystallization so tenaciously that it is not removed by drying to constant weight in a vacuum desiccator:

Found: N, 8.29; Br, 23.42; S, 9.79. Calculated for $C_9H_5O_4N_2BrS \cdot H_2O$: N, 8.31; Br, 23.71; S, 9.51.

Heated in a sealed capillary, it sublimes above 200° (uncor.), partly liquefies in the vicinity of 240° , resolidifies, darkens, softens and finally melts at about $285\text{--}286.5^\circ$ (uncor.). It dissolves easily in methyl or ethyl alcohol, or in water; but is practically insoluble in ether.

The filtrate from the first crystallization of the crude barium salt of this sulfo acid yielded additional amounts of barium phthalate on evaporation.

4-Quinazolone-2-Phthalines.—Eibner and his co-workers¹ found it impossible in several cases to obtain α -phthalines from their phthalones, and our experience with 4-quinazolone-2-phthalone was similar. We first heated the ammonium salt of the phthalone for 20 hours at 210° with excess of alcoholic ammonia and then, as no reaction was evident, opened the tube, added a little zinc chloride and a little more alcoholic ammonia, resealed and continued the heating for nearly 22 hours longer. There was evidence of some decomposition then, but we failed to isolate any phthaline.

Bis-(4-Quinazolone-2-)- β -Phthaline, $C_8H_5ON_2 \cdot CH : C \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ C_6H_4 \end{array} C : CH \cdot C_8H_5ON_2$.

—Equal amounts of phthalimide and 2-methyl-4-quinazolone were intimately mixed and the mixture heated. The mass melted to a yellowish brown liquid at about 225° , but no evolution of water occurred even at 245° . The addition of small amounts of zinc chloride, however, started the reaction immediately, and the heating was continued at $220\text{--}40^\circ$ for somewhat over two hours. When cold, the dark brown mass was pulverized and extracted repeatedly with boiling, dilute acetic acid. The combined extracts on cooling deposited a reddish brown powder and, without removing this precipitate, the solution was made faintly alkaline with ammonia. The precipitate was removed, redissolved in boiling, dilute acetic acid, reprecipitated with ammonia, washed with water, dried and analyzed:

Found: N, 16.38. Calculated for $C_{20}H_{17}O_2N_4$: N, 16.25.

The amount of material available was insufficient for a complete analysis, or for a thorough study of its properties, but we believe the substance to be the bis-quinazolone phthaline.

It is an orange-brown amorphous, or micro-crystalline, solid which

¹ *Ber.*, 37, 3605 (1904). *Chem. Ztg.*, 28, 1206 (1904).

when heated gradually darkens, sinters and finally forms a tar. It is soluble in alcohol, ether, dilute acetic acid, or ethyl acetate, the latter solution showing a greenish fluorescence. Its solution in dilute acetic acid acts as a powerful yellow dye, dyeing both natural and artificial silk a brilliant yellow, and unmordanted cotton thread a dull yellow.

4-Quinazolone-2-β-Phthaline, $C_9H_5ON_2 \cdot CH : C.CO.C_6H_4.NH$.—The crude product of the interaction of the quinazolone, phthalimide and zinc chloride, after extraction of the bis-quinazolone phthaline with boiling dilute acetic acid, was dissolved in boiling alcohol, filtered, and the filtrate concentrated. The orange-brown micro-crystalline precipitate which separated on cooling did not appear homogeneous under the microscope and yielded appreciable amounts of quinazolone phthalone on extraction with dilute ammonium hydroxide solution. The residue was then recrystallized from alcohol and analyzed:

Found: N, 14.73. Calculated for $C_{17}H_{11}O_2N_2$: N, 14.50.

The compound crystallizes from alcohol in very voluminous aggregates of orange-brown, microscopic prisms, which sublime above 250° , sintering and decomposing at about 338° (uncor.), and finally liquefying in the neighborhood of 349° (uncor.). It is easily soluble in nitrobenzene; moderately soluble in amyl alcohol; difficultly soluble in acetone, alcohol or chloroform; and practically insoluble in water or ether. With dilute potassium hydroxide solution, it forms an orange-brown, difficultly soluble, potassium salt.

Action of Succinic Anhydride upon 2-Methyl-4-Quinazolone.—Eibner and Lange¹ failed to get the succinone of quinaldine by the direct action of succinic anhydride, since the reaction was so vigorous that only a tarry mass resulted. They finally succeeded in obtaining it, however, by heating the succinimide condensation product with hydrochloric acid, the succinone showing the characteristic yellow color of these phthalones.

In our experiment, equimolecular amounts of 2-methyl-4-quinazolone and succinic anhydride were intimately mixed and the mixture heated. At $220-30^\circ$ the mixture melted to a dark brownish red liquid and began to boil from escaping steam. After heating for three hours, the melt was allowed to cool, and the black vitreous mass pulverized, boiled with dilute sodium hydroxide solution, filtered, and the dark brown filtrate acidified with acetic acid. The dark brown precipitate thus obtained was dissolved in boiling alcohol, the solution treated with bone-black, and the light yellow filtrate concentrated. On cooling, glistening gray leaflets separated, which were again treated with bone-black in alcoholic solution and crystallized to constant melting point:

Found: N, 11.73. Calculated for the succinone, $C_{13}H_{10}O_2N_2$: N, 11.57.

¹ *Loc. cit.*

The purified substance when crystallized rapidly from alcohol separates in short, colorless microscopic prisms. On slow crystallization, some also separates in large, thin, feathery plates of pearly luster. It melts with decomposition at about $274-7^{\circ}$ (uncor.). It dissolves in concentrated sulfuric acid to a colorless solution, and also forms a colorless salt with an absolute alcohol solution of sodium ethylate which dissolves on dilution.

In spite of the analytical result above, the absence of color from the compound and its salts renders it very doubtful as to whether it is a phthalone at all. Unfortunately, not enough of the material was isolated for a complete analysis.

6-Nitro-4-Quinazolone-2-Phthalone, $\text{O}_2\text{N} \cdot \text{C}_8\text{H}_4\text{ON}_2 \cdot \text{C}_6\text{H}_5\text{O}_2\text{N}$.—6-Nitro-2-methyl-4-quinazolone was heated with an equal weight of phthalic anhydride for two hours at about 210° . A pasty mass was obtained which soon turned yellow. The cold melt was pulverized, thoroughly extracted with boiling water, the residue dried and then heated for half an hour with an absolute alcoholic solution of sodium ethylate. The chocolate-colored salt thus obtained was removed by filtration from the well-cooled solution. By using a sodium hydroxide solution of the proper concentration, certain dark colored impurities were extracted without dissolving much of the salt. The crude orange-red salt remaining was then washed through the filter with boiling water, and on acidifying the filtrate with acetic acid the light yellow nitro-phthalone precipitated. This was crystallized twice from nitrobenzene, washed thoroughly with alcohol, glacial acetic acid and ether, dried at 110° and analyzed:

Found: N, 12.83. Calculated for $\text{C}_{17}\text{H}_9\text{O}_5\text{N}_3$: N, 12.54.

The purified substance forms ochre-yellow, minute crystals, not melting below 355° (uncor.). It is very difficultly soluble in hot, glacial acetic acid, and practically insoluble in cold alcohol, ether, or water. The orange-red water-soluble sodium salt slowly hydrolyzes to the phthalone when its aqueous solution is boiled. The phthalone boiled with an absolute alcohol solution of sodium ethylate forms a drab salt, which changes to orange on the addition of a little water, and deposits the orange-red salt when this diluted solution is boiled. Eibner and Lange¹ found that nitro-quinophthalone lost its nitro group when boiled with dilute acids or alkalies, but we did not observe anything of this kind with the nitro-quinazolone phthalone above.

7 - Acetamino - 4 - Quinazolone - 2 - Phthalone, $\text{CH}_3\text{CONH} \cdot \text{C}_8\text{H}_4\text{ON}_2 \cdot \text{CH} : \text{C}_2\text{O}_2 : \text{C}_6\text{H}_4$.—7-Acetamino-2-methyl-4-quinazolone² was heated with slightly more than an equal weight of phthalic anhydride for three hours at about 220° . Slow evolution of water began at about 190° and con-

¹ *Loc. cit.*

² Bogert, Amend and Chambers, *THIS JOURNAL*, 32, 1301 (1910).

tinued as the temperature rose, and the mass which was pasty at first gradually hardened and became a yellowish brown. The cold melt was pulverized and thoroughly extracted with boiling water, to remove unchanged initial materials and then washed with a little cold alcohol to remove a brown impurity. The residue was heated for half an hour with an absolute alcohol solution of sodium ethylate, the mixture allowed to cool, the dark brownish red salt filtered out and ground to a paste with hot water, forming a yellowish brown, difficultly soluble salt, which was converted to the phthalone by acidifying with acetic acid. The crude phthalone was washed thoroughly with hot water, dried, and boiled ten minutes with acetic anhydride and a little fused sodium acetate, to reacylate any liberated amine. The mixture was diluted with a large volume of water, boiled, and allowed to cool. The flocculent precipitate was filtered out, washed with hot water, recrystallized twice from glacial acetic acid, and analyzed:

Found: N, 12.28. Calculated for $C_{10}H_{10}O_4N_2$: N, 12.11.

It separates from glacial acetic acid in a voluminous mass of minute, glistening, bright yellow plates, which do not melt below 356° (uncor.). It is soluble in hot nitrobenzene or hot amyl alcohol, but insoluble in ether. Attempts to split off the acetyl group by alkali or acid resulted unsatisfactorily, the products showing a nitrogen content between that of the acetamino and that of the amino compound. This was wholly unexpected, as the 7-acetamino-2-methyl-4-quinazolone itself can be de-acetylated quite easily.

2-Methyl-3-Ethyl-4-Quinazolone, $C_2H_5.N.CO.C_6H_4.N : C.CH_3$, was prepared by slowly adding acetanthranil to an excess of a hot (approximately 25%) aqueous solution of ethylamine containing a few drops of potassium hydroxide solution, boiling for a few minutes and then allowing the solution to cool. An oil separated which finally solidified, and was then recrystallized twice from dilute alcohol, dried to constant weight in a vacuum desiccator and analyzed:

Found: N, 15.30. Calculated for $C_{11}H_{12}ON_2$: N, 14.89.

Fine colorless needles, which melt at 67° (cor.). It is very easily soluble in alcohol, ether, acetone, chloroform or benzene; less readily soluble in hot water or petroleum ether.

Its *chlorplatinate* forms orange needles, decomposing at about 229° (uncor.):

Found: Pt, 24.75. Calculated for $(C_{11}H_{12}ON_2)_2H_2PtCl_6$: Pt, 24.83.

It is difficultly soluble in alcohol, more readily soluble in water.

Acetanthranilic Ethylamide, $C_2H_5NHCO.C_6H_4.NHCOCH_3$, was isolated as a by-product in the course of one of the experiments for the preparation of the 2-methyl-3-ethyl-4-quinazolone when no potassium hydroxide

was added to the ethyl amine solution. It was easily separated from the quinazolone by fractional crystallization from dilute alcohol, in which the amide is much the less soluble. It was recrystallized twice from alcohol and analyzed:

Found: N, 13.83. Calculated for $C_{11}H_{14}O_2N_2$: N, 13.59.

It forms transparent prismatic plates, m. p. $139.5-140.5^\circ$ (cor.), which are easily soluble in alcohol or chloroform; moderately soluble in ether, carbon tetrachloride, benzene or hot water.

3-Ethyl-4-Quinazolone-2-Phthalone, $C_2H_5 \cdot C_8H_4ON_2 \cdot C_6H_5O_2$.—When a mixture of about equal weights of 2-methyl-3-ethyl-4-quinazolone and phthalic anhydride was heated, a clear yellowish brown melt resulted at about 160° . Steam began to escape when the temperature was raised to 190° and the melt boiled vigorously at 200° (uncor.). Heating was continued at the latter temperature for five hours and a half. The product was a dark red, translucent viscous mass which, when left in contact with alcohol for several days at room temperature, gradually disintegrated, giving a deep red solution and depositing lemon-yellow needles. The latter were filtered off and washed with a little alcohol. An additional crop of these yellow needles was recovered by concentrating the mother-liquor. The final filtrate on dilution with water deposited a dark red oil. The yellow needles were warmed with an absolute alcohol solution of sodium ethylate for half an hour at 100° , and sufficient water then added to bring all into solution. This deep orange solution of the sodium salt was acidified with acetic acid and the light yellow phthalone precipitated. The precipitate was thoroughly washed with hot water and hot, very dilute acetic acid, and dried. Yield, 14.3%. The product was tribo-electric. On recrystallization from strong acetic acid, it lost its tribo-electric properties:

Found: N, 9.04, 9.05. Calculated for $C_{18}H_{11}O_3N_2$: N, 8.81.

From alcohol it crystallizes in beautiful bright yellow, glistening, prismatic needles, showing a faint greenish fluorescence. It melts at 198.5° (cor.), and is extremely soluble in chloroform; easily soluble in glacial acetic acid; moderately soluble in alcohol or strong acetic acid; difficultly soluble in methyl alcohol or acetone; and very difficultly soluble in ether.

By the action of heat alone, only a very slight condensation was brought about between phthalic anhydride and 2,3-dimethyl-4-quinazolone. A mixture of yellow and brown crystals was isolated from the melt, but the amount was too small to enable us to separate any pure phthalone. When the condensation was conducted in presence of zinc chloride, only a tarry mass was obtained.

2-Methyl-3-phenyl-4-quinazolone and phthalic anhydride, when condensed in presence of zinc chloride, likewise gave a tar, from which no

pure phthalone could be recovered. In absence of zinc chloride, the effort to get the phthalone also proved futile.

2-Methyl-3-acetamino-4-quinazolone¹ and phthalic anhydride condensed at 220° with evolution of water, forming a violet-brown substance which dissolved in alkalis to a brown solution, and from which it was reprecipitated by acetic or dilute sulfuric acid. Not enough of the material was obtained for further investigation.

NEW YORK CITY.

THE LEAF-OIL OF THE WASHINGTON CEDAR (*THUJA PLICATA*).

BY ROBERT EVSTAFIEFF ROSE AND CARL LIVINGSTON.

Received December 12, 1911.

The leaf oil of the Washington cedar (*thuja plicata*) has not been examined chemically save by I. W. Brandel who published a short note on its composition.² The investigation referred to being only in the nature of an approximate analysis, the authors thought it advisable to undertake a more detailed study of the oil, the results of which follow: It may be mentioned that the conclusions reached differ very appreciably from those of Brandel.³

On steam distillation at 100°, the leaves and twigs of *thuja plicata* yield about 1% of a clear, light yellow oil which possesses the characteristic odor of cedar boughs.

The following constants were found: D_{20° , 0.913; $n_D^{20^\circ}$, 1.4552; $[\alpha]_D^{20^\circ}$, -4.77°; acid number, 0.518; ester number, 2.28; saponification number, 2.8; acetylation number, 8.8.

An elementary analysis showed the absence of sulfur and nitrogen, while the percentage composition (C = 78.6; H = 10.4) agreed very closely with that of a bicyclic ketone, $C_{10}H_{16}O$ (calc. C = 78.04; H = 10.52). The oil contained no phenols and was soluble in all proportions in anhydrous organic solvents and in 70% ethyl alcohol.

A fractional distillation under reduced pressure showed that 85% of the oil boiled between 100 and 110° under 40 mm. The small fraction (about 4%) boiling below 100°/40 mm. gave D_{20° 0.851, $n_D^{20^\circ}$ 1.4609, $[\alpha]_D^{20^\circ}$ +36.8° and was chiefly composed of pinene, which was identified by the preparation of the nitrosochloride melting at 103°. The main fraction was repeatedly distilled and yielded thus an oil boiling at 103–104° under 40 mm., which was found to be thujone by the following constants and derivatives:

D_{20° , 0.9152; $n_D^{20^\circ}$, 1.4530; $[\alpha]_D^{20^\circ}$, -11.58°.

¹ Bogert and Gortner, THIS JOURNAL, 31, 946 (1909).

² Pharm. Rev., 26, 248.

³ Loc. cit.

Derivatives: tribromide, melting point $121-122^{\circ}$;¹ semicarbazone,² melting point $186-188^{\circ}$ (from methyl alcohol); tanacetone keto carbonic acid,³ melting point $75-76^{\circ}$.

The reaction with hydroxylamine gave an oily oxime which crystallized only partially after standing for several months, which fact, together with the observed laevo rotation—a rotation, it may be noted, slightly higher than any previously recorded—further characterized the substance as α -thujone.

The fraction boiling from $100-103^{\circ}/40$ mm. (D_{20}° , 0.8975; n_D^{20} , 1.4549; $[\alpha]_D^{20}$, -0.62°) was tested for fenchone, since that ketone has been isolated from the oil of *thuja occidentalis*. Using Wallach's method—oxidation with potassium permanganate, steam distillation, further oxidation with concentrated nitric acid, and recovery of the unaltered fenchone by distillation in steam—only a few drops of oil were obtained which were heavier than water and in which no fenchone was found. An attempt to prepare the oxime of the ketone after removal of the thujone by oxidation was equally unsuccessful. The authors conclude, therefore, that fenchone is not present as stated by Brandel.⁴

The residue (about 5%) boiling above $110^{\circ}/40$ mm. (D_{20}° , 0.980) was dark brown in color and had an odor of stewed prunes. This was hydrolyzed with alcoholic potash, steam distilled, and fractionated. A light yellow oil was obtained whose constants show it to be tanacetyl alcohol (D_{25}° , 0.9266; n_D^{25} , 1.46207; $[\alpha]_D^{25}$, $+29.8$; boiling point at 757 mm., $210-220^{\circ}$), probably present as acetate in the original oil.

From the above results, the authors conclude that the volatil oil of *thuja plicata* is composed of 80–85% thujone, 3–5% pinene, 1–2% tanacetyl acetate, 1–3% tanacetyl alcohol, leaving about 10% to be accounted for by loss due to formation of resin during distillation and experimental losses.

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[CONTRIBUTION FROM THE CONTRACTS LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE UNIFICATION OF REDUCING SUGAR METHODS. (A CORRECTION.)

BY PERCY H. WALKER.

Mr. M. N. Straughn, of the sugar laboratory of this bureau, has recently called attention to certain errors in the tables for lactose given in the

¹ Wallach, *Ann.*, 275, 179; 286, 109.

² Wallach, *Ibid.*, 336, 251.

³ Wallach, *Ibid.*, 272, 113; 275, 164. Semmler, *Ber.*, 25, 3307. Tiemann and Semmler, *Ber.*, 30, 431.

⁴ *Loc. cit.*

article published in *THIS JOURNAL*, 29, 541-554. Table III, on page 544, giving a comparison of determined and calculated figures on cuprous oxide for definite amounts of sugar, is correct, while Table IV, beginning on page 545 and giving the amounts of sugar for each milligram of cuprous oxide from 10-490, contains errors in the lactose column, the figures disagreeing with the preceding table. These tables were used in compiling the tables given in Bureau of Chemistry, *Bull.* 107, revised,¹ pages 243-251, which have been used quite generally for several years, and Mr. Straughn has been the first to call attention to this discrepancy. A careful examination of the original notes showed that there are two misprints in the values given in the Journal for a , b , and c , to be substituted in the equation $y = a + bx + cx^2$ where y = cuprous oxide and x = reducing sugar, the values of a , b , and c being calculated from the determinations made by the method of least squares as used by Allihn.² The original article gives the accepted values for lactose as follows:

$$a = 4.1759$$

$$b = 1.148697$$

$$c = 0.00009$$

The true values which were actually used in making the calculations are:

$$a = 4.1759$$

$$b = 1.48697$$

$$c = -0.00009$$

As before stated, the calculations appearing in Table III are correct, but in Table IV errors occur in the figures in columns 3, 4, and 5, while the figures in columns 6 and 7 are correct. The values in column 4 were calculated from the equation for certain fixed weights of cuprous oxide, and the intermediate values obtained by interpolation, columns 3 and 5 being then derived in a similar manner from column 4. Table I of this article shows a comparison of the values as given in Tables III and IV of the original article and also the corresponding values taken from the recalculated table.

It is impossible to say how the errors occurred, since the sheets on which the calculations were made were destroyed shortly after the article was published. It is obvious, however, that such errors are entirely too great to appear in a table of this character; the figures have, therefore, been recalculated from the original data, and in Table II the corrected values for anhydrous lactose ($C_{12}H_{22}O_{11}$), and crystallized lactose³

¹ The final tables as given in Bureau of Chemistry, *Bull.* 107, revised, Official and Provisional Methods of Analysis, pp. 243-251, also call for the corrections as shown in Table II.

² *J. prakt. Chem.*, 22, 46 (1880).

³ The lactose actually used in determining the values from which these tables are calculated was crystallized lactose of the composition $C_{12}H_{22}O_{11} \cdot \frac{1}{2}H_2O$.

($C_{12}H_{22}O_{11}^{1/2}H_2O$), and crystallized lactose ($C_{12}H_{22}O_{11}H_2O$) are given for each milligram of cuprous oxide from 10 to 490.

TABLE I.—SHOWING MILLIGRAMS OF CUPROUS OXIDE AS DETERMINED, AS ORIGINALLY CALCULATED, AND AS RECALCULATED.

(1) Milligrams of lactose ($C_{12}H_{22}O_{11}$ + $\frac{1}{2}H_2O$).	Milligrams of Cu_2O .			
	(2) Actually obtained in work.	(3) Calculated from equa- tion $y = a +$ $bx + cx^2$.	(4) As given in original table.	(5) As given in recalcu- lated table.
20.....	33.0	33.9	33.9	33.9
40.....	63.2	63.5	63.7	63.5
60.....	92.9	93.1	93.4	93.0
80.....	123.9	122.6	123.1	122.6
100.....	154.1	152.0	153.0	152.0
120.....	180.6	181.3	182.7	181.3
140.....	210.7	210.6	212.6	210.6
160.....	239.4	239.8	242.3	239.7
180.....	268.0	269.0	272.1	268.9
200.....	297.1	298.0	302.0	298.0
220.....	326.8	327.0	331.7	326.9
240.....	356.1	355.9	361.6	355.9
260.....	384.4	384.7	391.4	384.7
280.....	413.9	413.5	421.3	413.4
300.....	443.1	442.2	451.1	442.1
320.....	470.3	470.8	481.0	470.7

Columns 1, 2, and 3 are taken from Table III, original article, THIS JOURNAL, 29, 544 (1907).

Column 4 is taken from Table IV of the original article and as given in Bureau of Chemistry, Bull. 107, revised, pp. 243-251.

Column 5 is taken from Table II of this article.

TABLE II.—TABLE FOR CALCULATING LACTOSE.
[Expressed in milligrams.]

Cu- prous oxide (Cu_2O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu_2O).	Copper (Cu).	Lactose.		
		($C_{12}H_{22}O_{11}$).	($C_{12}H_{22}O_{11}$ + $\frac{1}{2}H_2O$).	($C_{12}H_{22}O_{11}H_2O$).			($C_{12}H_{22}O_{11}$).	($C_{12}H_{22}O_{11}$ + $\frac{1}{2}H_2O$).	($C_{12}H_{22}O_{11}H_2O$).
10	8.9	3.8	3.9	4.0	25	22.2	13.7	14.0	14.4
11	9.8	4.5	4.6	4.7	26	23.1	14.3	14.7	15.1
12	10.7	5.1	5.3	5.4	27	24.0	15.0	15.4	15.8
13	11.5	5.8	5.9	6.1	28	24.9	15.6	16.1	16.5
14	12.4	6.4	6.6	6.8	29	25.8	16.3	16.7	17.1
15	13.3	7.1	7.3	7.5	30	26.6	16.9	17.4	17.8
16	14.2	7.8	8.0	8.2	31	27.5	17.6	18.1	18.5
17	15.1	8.4	8.6	8.9	32	28.4	18.3	18.7	19.2
18	16.0	9.1	9.3	9.5	33	29.3	18.9	19.4	19.9
19	16.9	9.7	10.0	10.2	34	30.2	19.6	20.1	20.6
20	17.8	10.4	10.7	10.9	35	31.1	20.2	20.8	21.3
21	18.7	11.0	11.3	11.6	36	32.0	20.9	21.4	22.0
22	19.5	11.7	12.0	12.3	37	32.9	21.5	22.1	22.7
23	20.4	12.3	12.7	13.0	38	33.8	22.2	22.8	23.4
24	21.3	13.0	13.4	13.7	39	34.6	22.8	23.5	24.1

TABLE II (Continued).

Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.		
		(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).			(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).
40	35.5	23.5	24.1	24.8	85	75.5	53.1	54.6	56.0
41	36.4	24.2	24.8	25.4	86	76.4	53.8	55.2	56.6
42	37.3	24.8	25.5	26.1	87	77.3	54.5	55.9	57.3
43	38.2	25.5	26.2	26.8	88	78.2	55.1	56.6	58.0
44	39.1	26.1	26.8	27.5	89	79.1	55.8	57.3	58.7
45	40.0	26.8	27.5	28.2	90	79.9	56.4	58.0	59.4
46	40.9	27.4	28.2	28.9	91	80.8	57.1	58.6	60.1
47	41.7	28.1	28.9	29.6	92	81.7	57.8	59.3	60.8
48	42.6	28.7	29.5	30.3	93	82.6	58.4	60.0	61.5
49	43.5	29.4	30.2	31.0	94	83.5	59.1	60.7	62.2
50	44.4	30.1	30.9	31.7	95	84.4	59.7	61.3	62.9
51	45.3	30.7	31.5	32.4	96	85.3	60.4	62.0	63.6
52	46.2	31.4	32.2	33.0	97	86.2	61.1	62.7	64.3
53	47.1	32.1	32.9	33.7	98	87.0	61.7	63.4	65.0
54	48.0	32.7	33.6	34.4	99	87.9	62.4	64.0	65.7
55	48.9	33.4	34.3	35.1	100	88.8	63.0	64.7	66.4
56	49.7	34.0	34.9	35.8	101	89.7	63.7	65.4	67.1
57	50.6	34.7	35.6	36.5	102	90.6	64.4	66.1	67.8
58	51.5	35.4	36.3	37.2	103	91.5	65.0	66.7	68.5
59	52.4	36.0	37.0	37.9	104	92.4	65.7	67.4	69.1
60	53.3	36.7	37.6	38.6	105	93.3	66.4	68.1	69.8
61	54.2	37.3	38.3	39.3	106	94.2	67.0	68.8	70.5
62	55.1	38.0	39.0	40.0	107	95.0	67.7	69.5	71.2
63	56.0	38.6	39.7	40.7	108	95.9	68.3	70.1	71.9
64	56.8	39.3	40.3	41.4	109	96.8	69.0	70.8	72.6
65	57.7	40.0	41.0	42.1	110	97.7	69.7	71.5	73.3
66	58.6	40.6	41.7	42.8	111	98.6	70.3	72.2	74.0
67	59.5	41.3	42.4	43.5	112	99.5	71.0	72.8	74.7
68	60.4	41.9	43.1	44.2	113	100.4	71.6	73.5	75.4
69	61.3	42.6	43.7	44.8	114	101.3	72.3	74.2	76.1
70	62.2	43.3	44.4	45.5	115	102.1	73.0	74.9	76.8
71	63.1	43.9	45.1	46.2	116	103.0	73.6	75.6	77.5
72	64.0	44.6	45.8	46.9	117	103.9	74.3	76.2	78.2
73	64.8	45.2	46.4	47.6	118	104.8	75.0	76.9	78.9
74	65.7	45.9	47.1	48.3	119	105.7	75.6	77.6	79.6
75	66.6	46.6	47.8	49.0	120	106.6	76.3	78.3	80.3
76	67.5	47.2	48.5	49.7	121	107.5	76.9	79.0	81.0
77	68.4	47.9	49.1	50.4	122	108.4	77.6	79.6	81.7
78	69.3	48.5	49.8	51.1	123	109.3	78.3	80.3	82.4
79	70.2	49.2	50.5	51.8	124	110.1	78.9	81.0	83.1
80	71.1	49.9	51.2	52.5	125	111.0	79.6	81.7	83.8
81	71.9	50.5	51.9	53.2	126	111.9	80.3	82.4	84.5
82	72.8	51.2	52.5	53.9	127	112.8	80.9	83.0	85.2
83	73.7	51.8	53.2	54.6	128	113.7	81.6	83.7	85.9
84	74.6	52.5	53.9	55.3	129	114.6	82.2	84.4	86.6

TABLE II (Continued).

Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.		
		(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).			(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).
130	115.5	82.9	85.1	87.3	175	155.4	112.8	115.7	118.7
131	116.4	83.6	85.7	88.0	176	156.3	113.4	116.4	119.4
132	117.2	84.2	86.4	88.7	177	157.2	114.1	117.1	120.1
133	118.1	84.9	87.1	89.4	178	158.1	114.8	117.8	120.8
134	119.0	85.5	87.8	90.1	179	159.0	115.4	118.4	121.5
135	119.9	86.2	88.5	90.8	180	159.9	116.1	119.1	122.2
136	120.8	86.9	89.1	91.5	181	160.8	116.7	119.8	122.9
137	121.7	87.5	89.8	92.1	182	161.7	117.4	120.5	123.6
138	122.6	88.2	90.5	92.8	183	162.5	118.1	121.2	124.3
139	123.5	88.9	91.2	93.5	184	163.4	118.7	121.8	125.0
140	124.4	89.5	91.9	94.2	185	164.3	119.4	122.5	125.7
141	125.2	90.2	92.5	94.9	186	165.2	120.1	123.2	126.4
142	126.1	90.8	93.2	95.6	187	166.1	120.7	123.9	127.1
143	127.0	91.5	93.9	96.3	188	167.0	121.4	124.6	127.8
144	127.9	92.2	94.6	97.0	189	167.9	122.1	125.3	128.5
145	128.8	92.8	95.3	97.7	190	168.8	122.7	125.9	129.2
146	129.7	93.5	95.9	98.4	191	169.7	123.4	126.6	129.9
147	130.6	94.2	96.6	99.1	192	170.5	124.1	127.3	130.6
148	131.5	94.8	97.3	99.8	193	171.4	124.7	128.0	131.3
149	132.3	95.5	98.0	100.5	194	172.3	125.4	128.7	132.0
150	133.2	96.1	98.7	101.2	195	173.2	126.1	129.4	132.7
151	134.1	96.8	99.3	101.9	196	174.1	126.7	130.0	133.4
152	135.0	97.5	100.0	102.6	197	175.0	127.4	130.7	134.1
153	135.9	98.1	100.7	103.3	198	175.9	128.1	131.4	134.8
154	136.8	98.8	101.4	104.0	199	176.8	128.7	132.1	135.5
155	137.7	99.5	102.1	104.7	200	177.6	129.4	132.8	136.2
156	138.6	100.1	102.8	105.4	201	178.5	130.0	133.5	136.9
157	139.5	100.8	103.4	106.1	202	179.4	130.7	134.1	137.6
158	140.3	101.5	104.1	106.8	203	180.3	131.4	134.8	138.3
159	141.2	102.1	104.8	107.5	204	181.2	132.0	135.5	139.0
160	142.1	102.8	105.5	108.2	205	182.1	132.7	136.2	139.7
161	143.0	103.4	106.2	108.9	206	183.0	133.4	136.9	140.4
162	143.9	104.1	106.8	109.6	207	183.9	134.0	137.6	141.1
163	144.8	104.8	107.5	110.3	208	184.8	134.7	138.3	141.8
164	145.7	105.4	108.2	111.0	209	185.6	135.4	138.9	142.5
165	146.6	106.1	108.9	111.7	210	186.5	136.0	139.6	143.2
166	147.4	106.8	109.6	112.4	211	187.4	136.7	140.3	143.9
167	148.3	107.4	110.3	113.1	212	188.3	137.4	141.0	144.6
168	149.2	108.1	110.9	113.8	213	189.2	138.0	141.7	145.3
169	150.1	108.8	111.6	114.5	214	190.1	138.7	142.4	146.0
170	151.0	109.4	112.3	115.2	215	191.0	139.4	143.0	146.7
171	151.9	110.1	113.0	115.9	216	191.9	140.0	143.7	147.4
172	152.8	110.8	113.7	116.6	217	192.7	140.7	144.4	148.1
173	153.7	111.4	114.3	117.3	218	193.6	141.4	145.1	148.8
174	154.6	112.1	115.0	118.0	219	194.5	142.0	145.8	149.5

TABLE II (Continued).

Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.		
		(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).			(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).
220	195.4	142.7	146.5	150.2	265	235.4	172.8	177.3	181.9
221	196.3	143.4	147.2	150.9	266	236.3	173.5	178.0	182.6
222	197.2	144.0	147.8	151.6	267	237.2	174.1	178.7	183.3
223	198.1	144.7	148.5	152.3	268	238.0	174.8	179.4	184.0
224	199.0	145.4	149.2	153.0	269	238.9	175.5	180.1	184.7
225	199.8	146.0	149.9	153.7	270	239.8	176.1	180.8	185.4
226	200.7	146.7	150.6	154.4	271	240.7	176.8	181.5	186.1
227	201.6	147.4	151.3	155.1	272	241.6	177.5	182.1	186.8
228	202.5	148.0	152.0	155.8	273	242.5	178.1	182.8	187.5
229	203.4	148.7	152.6	156.5	274	243.4	178.8	183.5	188.2
230	204.3	149.4	153.3	157.2	275	244.3	179.5	184.2	188.9
231	205.2	150.0	154.0	157.9	276	245.1	180.2	184.9	189.6
232	206.1	150.7	154.7	158.6	277	246.0	180.8	185.6	190.3
233	207.0	151.4	155.4	159.3	278	246.9	181.5	186.3	191.0
234	207.8	152.0	156.1	160.0	279	247.8	182.2	187.0	191.7
235	208.7	152.7	156.7	160.7	280	248.7	182.8	187.7	192.4
236	209.6	153.4	157.4	161.4	281	249.6	183.5	188.3	193.1
237	210.5	154.0	158.1	162.1	282	250.5	184.2	189.0	193.9
238	211.4	154.7	158.8	162.8	283	251.4	184.8	189.7	194.6
239	212.3	155.4	159.5	163.5	284	252.3	185.5	190.4	195.3
240	213.2	156.1	160.2	164.3	285	253.1	186.2	191.1	196.0
241	214.1	156.7	160.9	165.0	286	254.0	186.9	191.8	196.7
242	214.9	157.4	161.5	165.7	287	254.9	187.5	192.5	197.4
243	215.8	158.1	162.2	166.4	288	255.8	188.2	193.2	198.1
244	216.7	158.7	162.9	167.1	289	256.7	188.9	193.8	198.8
245	217.6	159.4	163.6	167.8	290	257.6	189.5	194.5	199.5
246	218.5	160.1	164.3	168.5	291	258.5	190.2	195.2	200.2
247	219.4	160.7	165.0	169.2	292	259.4	190.9	195.9	200.9
248	220.3	161.4	165.7	169.9	293	260.2	191.5	196.6	201.6
249	221.2	162.1	166.3	170.6	294	261.1	192.2	197.3	202.3
250	222.1	162.7	167.0	171.3	295	262.0	192.9	198.0	203.0
251	222.9	163.4	167.7	172.0	296	262.9	193.6	198.7	203.7
252	223.8	164.1	168.4	172.7	297	263.8	194.2	199.3	204.4
253	224.7	164.7	169.1	173.4	298	264.7	194.9	200.0	205.1
254	225.6	165.4	169.8	174.1	299	265.6	195.6	200.7	205.8
255	226.5	166.1	170.5	174.8	300	266.5	196.2	201.4	206.6
256	227.4	166.8	171.1	175.5	301	267.4	196.9	202.1	207.3
257	228.3	167.4	171.8	176.2	302	268.2	197.6	202.8	208.0
258	229.2	168.1	172.5	176.9	303	269.1	198.3	203.5	208.7
259	230.0	168.8	173.2	177.6	304	270.0	198.9	204.2	209.4
260	230.9	169.4	173.9	178.3	305	270.9	199.6	204.9	210.1
261	231.8	170.1	174.6	179.0	306	271.8	200.3	205.5	210.8
262	232.7	170.8	175.3	179.8	307	272.7	201.0	206.2	211.5
263	233.6	171.4	176.0	180.5	308	273.6	201.6	206.9	212.2
264	234.5	172.1	176.6	181.2	309	274.5	202.3	207.6	212.9

TABLE II (Continued).

Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.		
		(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).			(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).
310	275.3	203.0	208.3	213.7	355	315.3	233.3	239.4	245.6
311	276.2	203.6	209.0	214.4	356	316.2	233.9	240.1	246.3
312	277.1	204.3	209.7	215.1	357	317.1	234.6	240.8	247.0
313	278.0	205.0	210.4	215.8	358	318.0	235.3	241.5	247.7
314	278.9	205.7	211.1	216.5	359	318.9	236.0	242.2	248.4
315	279.8	206.3	211.8	217.2	360	319.8	236.7	242.9	249.1
316	280.7	207.0	212.5	217.9	361	320.6	237.3	243.6	249.8
317	281.6	207.7	213.1	218.6	362	321.5	238.0	244.3	250.5
318	282.5	208.4	213.8	219.3	363	322.4	238.7	245.0	251.2
319	283.3	209.0	214.5	220.0	364	323.3	239.4	245.7	252.0
320	284.2	209.7	215.2	220.7	365	324.2	240.0	246.4	252.7
321	285.1	210.4	215.9	221.4	366	325.1	240.7	247.0	253.4
322	286.0	211.0	216.6	222.2	367	326.0	241.4	247.7	254.1
323	286.9	211.7	217.3	222.9	368	326.9	242.1	248.4	254.8
324	287.8	212.4	218.0	223.6	369	327.8	242.7	249.1	255.5
325	288.7	213.1	218.7	224.3	370	328.6	243.4	249.8	256.2
326	289.6	213.7	219.4	225.0	371	329.5	244.1	250.5	256.9
327	290.4	214.4	220.1	225.7	372	330.4	244.8	251.2	257.7
328	291.3	215.1	220.7	226.4	373	331.3	245.4	251.9	258.4
329	292.2	215.8	221.4	227.1	374	332.2	246.1	252.6	259.1
330	293.1	216.4	222.1	227.8	375	333.1	246.8	253.3	259.8
331	294.0	217.1	222.8	228.5	376	334.0	247.5	254.0	260.5
332	294.9	217.8	223.5	229.2	377	334.9	248.1	254.7	261.2
333	295.8	218.4	224.2	230.0	378	335.7	248.8	255.4	261.9
334	296.7	219.1	224.9	230.7	379	336.6	249.5	256.1	262.6
335	297.6	219.8	225.6	231.4	380	337.5	250.2	256.8	263.4
336	298.4	220.5	226.3	232.1	381	338.4	250.8	257.5	264.1
337	299.3	221.1	227.0	232.8	382	339.3	251.5	258.1	264.8
338	300.2	221.8	227.7	233.5	383	340.2	252.2	258.8	265.5
339	301.1	222.5	228.3	234.2	384	341.1	252.9	259.5	266.2
340	302.0	223.2	229.0	234.9	385	342.0	253.6	260.2	266.9
341	302.9	223.8	229.7	235.6	386	342.9	254.2	260.9	267.6
342	303.8	224.5	230.4	236.3	387	343.7	254.9	261.6	268.3
343	304.7	225.2	231.1	237.0	388	344.6	255.6	262.3	269.0
344	305.5	225.9	231.8	237.8	389	345.5	256.3	263.0	269.8
345	306.4	226.5	232.5	238.5	390	346.4	256.9	263.7	270.5
346	307.3	227.2	233.2	239.2	391	347.3	257.6	264.4	271.2
347	308.2	227.9	233.9	239.9	392	348.2	258.3	265.1	271.9
348	309.1	228.5	234.6	240.6	393	349.1	259.0	265.8	272.6
349	310.0	229.2	235.3	241.3	394	350.0	259.6	266.5	273.3
350	310.9	229.9	235.9	242.0	395	350.8	260.3	267.2	274.0
351	311.8	230.6	236.6	242.7	396	351.7	261.0	267.9	274.7
352	312.7	231.2	237.3	243.4	397	352.6	261.7	268.6	275.5
353	313.5	231.9	238.0	244.1	398	353.5	262.3	269.3	276.2
354	314.4	232.6	238.7	244.8	399	354.4	263.0	269.9	276.9

TABLE II (Continued).

Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.			Cu- prous oxide (Cu ₂ O).	Copper (Cu).	Lactose.		
		(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).			(C ₁₂ H ₂₂ O ₁₁).	(C ₁₂ H ₂₂ O ₁₁ ½H ₂ O).	(C ₁₂ H ₂₂ O ₁₁ H ₂ O).
400	355.3	263.7	270.6	277.6	445	395.3	294.2	302.0	309.7
401	356.2	264.4	271.3	278.3	446	396.1	294.9	302.7	310.5
402	357.1	265.0	272.0	279.0	447	397.0	295.6	303.4	311.2
403	358.0	265.7	272.7	279.7	448	397.9	296.3	304.1	311.9
404	358.8	266.4	273.4	280.4	449	398.8	297.0	304.8	312.6
405	359.7	267.1	274.1	281.1	450	399.7	297.6	305.5	313.3
406	360.6	267.8	274.8	281.9	451	400.6	298.3	306.2	314.0
407	361.5	268.4	275.5	282.6	452	401.5	299.0	306.9	314.7
408	362.4	269.1	276.2	283.3	453	402.4	299.7	307.6	315.5
409	363.3	269.8	276.9	284.0	454	403.3	300.4	308.3	316.2
410	364.2	270.5	277.6	284.7	455	404.1	301.1	309.0	316.9
411	365.1	271.2	278.3	285.4	456	405.0	301.7	309.7	317.6
412	365.9	271.8	279.0	286.2	457	405.9	302.4	310.4	318.3
413	366.8	272.5	279.7	286.9	458	406.8	303.1	311.1	319.0
414	367.7	273.2	280.4	287.6	459	407.7	303.8	311.8	319.8
415	368.6	273.9	281.1	288.3	460	408.6	304.5	312.5	320.5
416	369.5	274.6	281.8	289.0	461	409.5	305.1	313.2	321.2
417	370.4	275.2	282.5	289.7	462	410.4	305.8	313.9	321.9
418	371.3	275.9	283.2	290.4	463	411.2	306.5	314.6	322.6
419	372.2	276.6	283.9	291.2	464	412.1	307.2	315.3	323.4
420	373.1	277.3	284.6	291.9	465	413.0	307.9	316.0	324.1
421	373.9	277.9	285.3	292.6	466	413.9	308.6	316.7	324.8
422	374.8	278.6	286.0	293.3	467	414.8	309.2	317.4	325.5
423	375.7	279.3	286.7	294.0	468	415.7	309.9	318.1	326.2
424	376.6	280.0	287.4	294.7	469	416.6	310.6	318.8	326.9
425	377.5	280.7	288.1	295.4	470	417.5	311.3	319.5	327.7
426	378.4	281.3	288.8	296.2	471	418.4	312.0	320.2	328.4
427	379.3	282.0	289.4	296.9	472	419.2	312.6	320.9	329.1
428	380.2	282.7	290.1	297.6	473	420.1	313.3	321.6	329.8
429	381.0	283.4	290.8	298.3	474	421.0	314.0	322.3	330.5
430	381.9	284.1	291.5	299.0	475	421.9	314.7	323.0	331.3
431	382.8	284.7	292.2	299.7	476	422.8	315.4	323.7	332.0
432	383.7	285.4	292.9	300.5	477	423.7	316.1	324.4	332.7
433	384.6	286.1	293.6	301.2	478	424.6	316.7	325.1	333.4
434	385.5	286.8	294.3	301.9	479	425.5	317.4	325.8	334.1
435	386.4	287.5	295.0	302.6	480	426.3	318.1	326.5	334.8
436	387.3	288.1	295.7	303.3	481	427.2	318.8	327.2	335.6
437	388.2	288.8	296.4	304.0	482	428.1	319.5	327.9	336.3
438	389.0	289.5	297.1	304.7	483	429.0	320.1	328.6	337.0
439	389.9	290.2	297.8	305.5	484	429.9	320.8	329.3	337.7
440	390.8	290.9	298.5	306.2	485	430.8	321.5	330.0	338.4
441	391.7	291.5	299.5	306.9	486	431.7	322.2	330.7	339.1
442	392.6	292.2	299.9	307.6	487	432.6	322.9	331.4	339.9
443	393.5	292.9	300.6	308.3	488	433.5	323.6	332.1	340.6
444	394.4	293.6	301.3	309.0	489	434.3	324.2	332.8	341.3
					490	435.2	324.9	333.5	342.0

[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY, BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE.]

STUDIES ON CHICKEN FAT.

I. THE OCCURRENCE AND PERMANENCE OF LIPASE IN THE FAT OF THE COMMON FOWL (*Gallus domesticus*).

BY M. E. PENNINGTON AND J. S. HEPBURN.

II. THE OXIDATION OF CHICKEN FAT BY MEANS OF HYDROGEN PEROXIDE.

BY JOSEPH S. HEPBURN.

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I. The Occurrence and Permanence of Lipase in the Fat of the Common Fowl (*Gallus domesticus*).

Post-mortem changes in chicken fat include a pronounced increase in acidity, whether it takes place slowly, as when the fat is kept hard frozen, or more and more rapidly as the temperature rises above the congealing point of flesh.¹ Such an increase in the acidity of fats has generally been traced to the enzyme lipase, which is not only widely distributed in nature, but is one of the most resistant enzymes known. Hence this study was undertaken to determine its presence in chicken fats coming from varying sources and in those which had been hard frozen for considerable lengths of time. A review of the literature on lipase² revealed but one record of the observation of that enzyme in the common fowl; Kastle and Loevenhart³ found lipase in the liver of the chicken.

The technique is fairly simple. The crude abdominal fat is passed several times through a meat chopper, and its acidity is determined by the method of Pennington and Hepburn.⁴ A weighed sample of the ground fat is triturated in a mortar with sand and then extracted by trituration with water. The solution is poured through a strainer of wire gauze and then is filtered through absorbent cotton. The extraction is repeated several times and finally the insoluble matter is placed on a muslin filter and squeezed to remove the aqueous extract as far as possible; this filtrate also is strained through wire gauze and filtered through absorbent cotton. The quantity of water used for extraction is so regulated that the total volume of the filtrate in cubic centimeters is exactly 10 times the weight in grams of the crude fat used in making the extract.

Fifty cc. of the aqueous extract and 1 cc. of an ester (ethyl acetate, butyrate, or benzoate, or amyl salicylate) are placed in an Erlenmeyer

¹ U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 115, 57 (1908); and *Cir.*, 70 (1911). *Premier Congrès International du Froid, Rapports et Communications*, 2, 216 (1908). *THIS JOURNAL*, 32, 568 (1910).

² Hepburn, *J. Frank. Inst.*, 168, 429 (1909).

³ *Am. Chem. J.*, 24, 491 (1900).

⁴ *THIS JOURNAL*, 32, 568 (1910).

flask of 100 cc. capacity, 0.2 cc. of a 1% solution of phenolphthalein in alcohol are added, and the solution is neutralized. One cc. of toluene is used as a bactericide, and at intervals during the incubation more is added to replace that lost by evaporation. The flask and its contents are incubated at 40°—the optimum temperature for lipase¹—for periods of time varying between 24 and 168 hours, usually 72 hours. A 50 cc. sample of the aqueous extract is boiled, cooled to the temperature of the room, and run as a blank experiment in exactly the same manner as the determination proper. At the end of the incubation both determination and blank experiment are titrated with tenth-normal sodium hydroxide; the increase in acidity of the determination proper over the blank is due to the action of lipase.

The data of the preliminary experiments are given in Table I, page 212. Since lipase will produce a further increase in acidity, if the solution is neutralized at intervals and then subjected to further incubation, experiments of this type were carried out as one of the tests for lipase. Thus in Experiment 1021-2, in the lipolysis of ethyl butyrate, after 24 hours, the determination proper showed an acidity of 1.30 cc., and the blank of 0.15 cc.; therefore the acidity due to lipase was 1.15 cc.; in the second period of 24 hours, a further increase in the determination proper of 0.80 cc. and in the blank of 0.20 cc. occurred, giving an increase due to lipase of 0.60 cc. In the table the total hydrolysis in the total time is given.

The presence of lipase is shown by the following facts: (1) The acidity of the crude abdominal fat; (2) the hydrolysis of the various esters; (3) the further hydrolysis of the esters after neutralization during incubation; (4) the influence of chemical constitution on the rate of hydrolysis of the esters.

During both the preliminary and the final series of experiments, the rate of hydrolysis was greater in the case of the butyric ester than in that of the acetic, *i. e.*, the rate became greater as the carbon content of the fatty acid increased. Kastle and Loevenhart² have found this property to be characteristic of lipase.

The final series of experiments is a study of the comparative activity of the lipase in fresh chickens and in fowls kept for varying periods of time at different temperatures, from 5° F. as a minimum to 65-78° F. as a maximum. Throughout the entire series the period of incubation was constant, 72 hours. The samples included a chicken which had just been killed and from which the animal heat had not been lost; one kept in the chill room at 32° F. for 24 hours; birds from the West and South of known history at various stages of their marketing; and fowls kept

¹ Kastle and Loevenhart, *Am. Chem. J.*, 24, 491 (1900).

² *Ibid.*, 24, 491 (1900).

TABLE I.—THE OCCURRENCE OF LIPASE IN THE FAT OF CHICKENS.

Description and number of sample.	Acid value of crude abdominal fat.	Ester.	Period in hours in incu- bator at 40°.	Acidity: N/10 NaOH.		
				Determina- tion after incubation. cc.	Blank after incubation. cc.	Increase due to lipase. cc.
No. 1023-3, well-bled, sound western market chicken of known history, at end of retail period.....	2.80	Ethyl butyrate	24	2.00	1.00	1.00
No. 1021-2, undrawn western chicken: 2 days in chillroom, 28-36° F.; 7 days in freezer, 5- 19° F.; 7 days in refrigerator car, 31-37° F.; 9 days at wholesaler's, 39-43° F.; 4 days at retailer's, 28-66° F.....	3.53	Ethyl butyrate	{ 24	1.30	0.15	1.15
			{ 48	2.10	0.35	1.75
			{ 120	2.65	0.50	2.15
			{ 144	2.80	0.50	2.30
No. 1021-3, wire-drawn western chicken: same history as 1021-2, undrawn, with two addi- tional days at retailer's at 28-66° F.....	2.78	{ Ethyl acetate	{ 72	1.85	0.30	1.55
			{ 96	2.10	0.45	1.65
		{ Ethyl butyrate	{ 72	2.15	0.35	1.80
			{ 96	2.25	0.40	1.85
		{ Amyl salicylate	{ 72	0.70	0.25	0.45
			{ 96	1.00	0.45	0.55
No. 1025-1, well-bled, sound western market chicken of known history, at beginning of retail period.....	1.97	{ Ethyl acetate	{ 72	1.65	0.50	1.15
			{ 144	2.20	0.60	1.60
		{ Ethyl butyrate	{ 72	0.75	0.20	0.55
			{ 144	0.95	0.30	0.65
		{ Amyl salicylate	{ 72	0.95	0.25	0.70
			{ 144	1.50	0.30	1.20

No. 343, broiling chickens of known history, hard frozen for 12 1/2 months.....	{	Ethyl acetate	24	1.45	0.45	1.00
			48	2.30	0.80	1.50
			120	2.85	1.10	1.75
			144	3.10	1.10	2.00
		Ethyl butyrate	168	3.60	1.10	2.50
			24	1.05	0.30	0.75
			48	2.05	0.45	1.60
			120	2.50	0.85	1.65
			144	2.65	0.85	1.80
		Ethyl benzoate	168	3.00	1.05	1.95
			24	0.90	0.55	0.35
		Amyl salicylate	48	1.90	0.90	1.00
No. 345, broiling chickens of known history, hard frozen for 13 months.....			120	3.05	1.40	1.65
{	Ethyl acetate	144	3.95	1.75	2.20	
		168	4.95	2.05	2.90	
		24	0.50	0.25	0.25	
		48	0.90	0.45	0.45	
	Ethyl butyrate	120	1.20	0.55	0.65	
		144	2.10	0.90	1.20	
		168	2.40	1.10	1.30	
		24	1.10	0.40	0.70	
{		48	1.65	0.65	1.00	
		24	1.00	0.30	0.70	
		48	1.75	0.45	1.30	

hard frozen for periods as long as 89 months. The chickens hard frozen for 16 months were market birds; those stored for longer periods were not marketable, and are only of scientific interest. The "green struck" chicken represents incipient putrefaction, while the bird kept at the temperature of the room for 7 days was in an advanced state of putrefaction.

In connection with this study of the action of prolonged freezing on the activity of lipase, it is interesting to review briefly the literature on the influence of low temperatures on enzyme action. Macfadyen and Rowland¹ found that zymase withstands for 24 hours the temperature of liquid air, while Buchner² prepared the same enzyme from yeast cells with the aid of solid carbon dioxide. The work of Kovchoff³ shows that the proteolytic enzyme of wheat, peas, and the tissue of *Vicia faba* retains its activity after these substances have been frozen for 24 hours. Pepsin and gastric juice are active at 0°, as shown by the work of Müller,⁴ Flaum,⁵ Fick and Murisier,⁶ and Hoppe-Seyler.⁷ Recently Oguro⁸ has demonstrated that pepsin and dilute hydrochloric acid digest ricin at temperatures of 8°, 5°, and 0°. Müller⁴ found that rennin resists a temperature of 0°. Kastle and Loevenhart⁹ state that the lipase of a pig pancreas retained 60% of its power to hydrolyze ethyl butyrate after that organ had been kept in cold storage for 7 days. A dry fat-free pancreas retained its lipolytic power in almost full strength for 7 weeks. Even a putrefying pancreas still possessed power to split the ester to a slight extent. Richardson¹⁰ states that the fat-splitting enzyme of the pancreatic juice "does still retain and show a little activity at freezing temperatures." His experiments were made on a mixture of fresh hog pancreas and neutral lard kept at a temperature of -9° to -12° for as long a period as 3 months.

The results of the final series of experiments are given in Table II. The lowest acidity of the crude fat and the least activity of the lipase is in the chicken retaining the animal heat; as the birds age after death the acidity of the crude fat becomes greater, as does also the activity of the enzyme; the increase is apparently dependent on both temperature and the period of keeping and has occurred even in the chicken

¹ *Lancet*, 78, [1] 849, 1130 (1900).

² *Die Zymasegarung*, 1903. Résumé by Bradbury in *J. Frank. Inst.*, 157, 41 (1904).

³ *Ber. bot. Ges.*, 25, 473 (1907).

⁴ *Arch. Hyg.*, 47, 127 (1903).

⁵ *Z. Biol. (N. F.)*, 10, 28, 433 (1891).

⁶ *Verh. Würzburger physiol.-med. Ges., N. F.*, 2, 122 (1872).

⁷ *Pflüger's Arch. ges. Physiol.*, 14, 395 (1877).

⁸ *Biochem. Z.*, 22, 278 (1909).

⁹ *Am. Chem. J.*, 24, 491 (1900).

¹⁰ *Premier Congrès International du Froid, Rapports et Communications*, 2, 315 (1908).

kept in the chill room at 32° F. for 24 hours. The three experiments, 2044-1, 1025-1, and 1021-3, represent western and southern chickens in various stages of their marketing; the highest acidity of the fat and the greatest activity of the lipase is found in the sample which has been on the market for the longest time. Likewise, the acidity of the fat and the activity of the enzyme is greater in the fowl in an advanced stage of putrefaction than in the "green struck" bird (incipient putrefaction). In the hard frozen samples the greatest activity of the lipase and the highest acidity of the fat is in the chicken kept hard frozen for 54 months; however, the enzyme was energetic in the bird hard frozen for 89 months. Therefore, lipase is able to resist prolonged freezing, even for a period of almost seven and a half years. The rate of increase in the acidity of the crude fat and in the activity of the enzyme is greatly decreased by prolonged hard freezing.

Apparently the crude fat of a chicken which has just been killed is almost, if not absolutely, neutral and contains lipase largely, if not entirely, as a zymogen, which is converted into the active form as the bird ages after death. Greater activity of the enzyme and a higher acidity of the crude fat usually occur as the period of keeping grows longer. This transition from zymogen to active enzyme is proved by the fact that extracts from aged birds possess greater lipolytic power than does the extract from the chicken retaining the animal heat.

Apart from the rendering active of a zymogen, an increase in the acidity of the fat may tend to increase the activity of the lipase toward the fat *in situ*. Thus Connstein, Hoyer, and Wartenberg,¹ who studied the lipase of the seed of the castor-oil plant (*Ricinus communis*), found that sulfuric, phosphoric, and acetic acids and sodium acid sulfate exert an accelerating action on the hydrolyses produced by lipase. However, they contend that certain of their experiments make it probable that these compounds act as catalytic agents for the active enzyme without functioning as activators for a zymogen. The optimum concentration of the reagents mentioned lies between tenth-normal and third-normal. Acids which are insoluble in water also exert an accelerating influence, although far larger quantities of such acids must be used to obtain the same result. Moreover, these investigators also discovered that the rate of hydrolysis becomes greater after the lipase of *Ricinus communis* has acted on a fat for some time. Hence, contrary to the habit of most enzymes, a piling up of the enzymic products of lipase is favorable to activity rather than depressing. Tanaka² has recently studied the use of acids in the cleavage of oil by means of the lipolytic enzyme of the castor-oil seed. For every acid there is an optimum amount, and a

¹ *Ber.*, 35, 3988 (1902).

² *J. Coll. Eng. Tokyo*, 5, 25-42; *C. A.*, 5, 2004 (1911).

TABLE II.—COMPARATIVE ACTIVITY OF LIPASE IN THE FAT OF CHICKENS KEPT UNDER VARYING CONDITIONS OF TEMPERATURE AND TIME.
(Period of incubation, 72 hours at 40°.)

Description and number of sample.	Acid value of crude abdominal fat.	Ester.	Acidity: N/10 NaOH.		
			Determina- tion after incubation. cc.	Blank after incubation. cc.	Increase due to lipase. cc.
No. 358, chicken retaining animal heat.....	0.20	Ethyl acetate	0.95	0.20	0.75
		Ethyl butyrate	0.80	0.20	0.60
		Ethyl benzoate	1.25	0.25	1.00
		Amyl salicylate	0.40	0.50	None
No. 359, chicken in chillroom at 32° F. for 24 hours ..	0.53	Ethyl acetate	1.35	0.20	1.15
		Ethyl butyrate	2.25	0.15	2.10
		Ethyl benzoate	3.10	1.85	1.25
		Amyl salicylate	0.80	0.20	0.60
No. 2044-1, dry-packed southern market chicken of known history at end of transportation period.....	1.08	Ethyl acetate	1.20	0.30	0.90
		Ethyl butyrate	1.90	0.30	1.60
		Ethyl benzoate	3.90	2.90	1.00
		Amyl salicylate	0.55	0.20	0.35
No. 1025-1, well-bled, sound western market chicken of known history, at beginning of retail period.....	1.97	Ethyl acetate	1.65	0.50	1.15
		Ethyl butyrate	0.75	0.20	0.55
		Amyl salicylate	0.95	0.25	0.70
No. 1021-3, wire-drawn western chicken: 2 days in chillroom, 28-36° F.; 7 days in freezer, 5-19° F.; 7 days in refrigerator car, 31-37° F.; 9 days at wholesaler's, 39-43° F.; 6 days at retailer's, 28- 66° F.....	2.78	Ethyl acetate	1.85	0.30	1.55
		Ethyl butyrate	2.15	0.35	1.80
		Amyl salicylate	0.70	0.25	0.45

No. 2053-2, dry-packed southern market chicken of known history, from commission merchant, "green struck"	3.20	{	Ethyl acetate	2.30	0.70	1.60
			Ethyl butyrate	3.15	0.30	2.85
			Ethyl benzoate	3.40	3.40	0.00
			Amyl salicylate	1.20	0.45	0.75
No. 361, chicken kept in room for 7 days; average temperature, 72.5° F.; minimum temperature, 67° F.; maximum temperature, 78° F.; advanced putrefaction.....	7.14	{	Ethyl acetate	2.70	1.10	1.60
			Ethyl butyrate	3.50	0.50	3.00
			Amyl salicylate	1.30	0.50	0.80
No. 1001-4, well-bled, sound, western market chicken of known history, hard frozen for 16 months.....	33.13	{	Ethyl acetate	3.20	1.10	2.10
			Ethyl butyrate	4.50	0.65	3.85
			Ethyl benzoate	5.00	1.30	3.70
			Amyl salicylate	1.95	0.70	1.25
No. 1001-4, badly bled, rubbed, western market chicken of known history, hard frozen for 16 months.....	34.85	{	Ethyl acetate	4.20	1.70	2.50
			Ethyl butyrate	5.70	1.10	4.60
No. 365, chicken of known history, hard frozen for 28 months.....	36.09		Ethyl butyrate	3.05	0.80	2.25
No. 367, chicken of known history, hard frozen for 29 months.....	6.62	{	Ethyl acetate	1.40	0.60	0.80
			Ethyl butyrate	1.50	0.40	1.10
No. 366, chicken of known history, hard frozen for 42 months.....	12.78	{	Ethyl acetate	2.10	0.85	1.25
			Ethyl butyrate	3.50	0.60	2.90
No. 372, chicken hard frozen for 54 months; history previous to freezing unknown.....	39.40	{	Ethyl acetate	5.65	2.75	2.90
			Ethyl butyrate	6.30	1.50	4.80
			Ethyl benzoate	4.20	1.80	2.40
			Amyl salicylate	8.50	4.00	4.50
No. 373, chicken hard frozen for 89 months; history previous to freezing unknown.....	32.88	{	Ethyl acetate	4.95	2.15	2.80
			Ethyl butyrate	5.90	1.35	4.55

further addition exerts a retarding influence. The function of the dilute acid is to combine with the basic constituents of the seed. Hence it is uncertain whether or not dilute acids can act as catalyzers for the active form of lipase.

In this and in other researches carried out in this laboratory it has been demonstrated that the acidity of the fat, both crude and extracted, increases after death, whether the chickens are kept at atmospheric temperatures or hard frozen for varying periods of time. During the course of this investigation the presence of active lipase has been demonstrated in the crude fat of chickens hard frozen, at various stages of marketing, and in early and advanced stages of putrefaction. Therefore the post-mortem hydrolysis of chicken fat *in situ* must be due in large part to the action of lipase.

The following conclusions are reached based on these studies:

- (1) Lipase occurs in the crude fat of chickens.
- (2) The fat of the fowl immediately after killing shows almost no lipolytic activity. It is therefore probable that the lipase during life exists in its zymogenic form.
- (3) As the chicken ages after death, the enzyme becomes active and the acidity of the fat increases. These changes occur less rapidly at temperatures below freezing than above the freezing point.
- (4) Lipase can resist prolonged freezing for as long a period as 89 months.
- (5) From the experiments cited it would appear that the post-mortem hydrolysis of chicken fat depends chiefly upon enzyme action.

II. The Oxidation of Chicken Fat by Means of Hydrogen Peroxide.

When the forces of nature, including bacteria, molds, yeasts, enzymes, air, light, and heat, act on fats and oils, the various constants undergo changes and an increase in the saponification number is usually accompanied by a decrease in the Hehner number, and *vice versa*. This phenomenon is due chiefly to the oxidation of the unsaturated acids at the double bonds.¹

However, when chickens are kept hard frozen, both the saponification number and the Hehner number experience a simultaneous change in the same direction.² For instance, nine analyses give a mean saponification number of 172.9 and a mean Hehner number of 81.27 for fresh roasters, while three analyses of undrawn roasters, kept hard frozen for 16 months, give a mean saponification number of 194.9 and a mean Hehner number of 91.67, the two constants having increased at the same

¹ Hepburn, *J. Frank. Inst.*, 168, 365, 421 (1909); 169, 23 (1910).

² Pennington, U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 115, 68, 73; *Premier Congrès International du Froid, Rapports et Communications*, 2, 216 (1908). Hepburn, *J. Frank. Inst.*, 171, 585 (1911).

time.¹ This form of fat decomposition must be due to oxidation of the carbon chain at or near the terminal carbon atoms.

The recent work of Dakin² upon the oxidation of the ammonium salts of the saturated fatty acids by means of hydrogen peroxide gave the idea which led to the present research. This investigator discovered that hydrogen peroxide reacts with the ammonium salts of saturated fatty acids at the temperature of boiling water with the evolution of carbon dioxide and the formation of lower fatty acids and of ketones—derived from β -ketonic acids by loss of carbon dioxide. In some cases aldehydes were also formed. Apparently oxidation occurs at the carbon atom in the β -position to the carboxyl group. It therefore seemed desirable to study the influence of oxidation with hydrogen peroxide upon the chemical constants of chicken fat and of stearic and oleic acids.

The fat was obtained from chickens of known history. All the samples, with two exceptions, were western birds at various stages of their marketing. Sample No. 360 was a chicken kept in a chillroom at 32° F. for 24 hours after killing and then analyzed, while Sample No. 343 was hard frozen for over a year. The crude abdominal fat was extracted with petroleum ether according to the method commonly used in this laboratory³ and was analyzed. The extracted fat was heated on the water bath for 7 hours with a 3% solution of hydrogen peroxide. Six molecules of peroxide were used for each molecule of fat, *i. e.*, two molecules of peroxide for each fatty acid radical. The fat was then separated from the aqueous layer and washed with boiling water until neither fat nor wash water contained peroxide, as was shown by their failure to respond to the potassium-bichromate-sulfuric-acid-ether test (formation of a blue color in the ether). The fat was then filtered through paper in a water oven at 100° with the utmost speed, and again analyzed. The methods of analysis were those of the Association of Official Agricultural Chemists.⁴ The iodine number was determined by the Hanus method. The analytical data are given in Table III.

It will be observed that the acidity always increased; the iodine number usually decreased, although occasionally it increased. The saponification number and the Hehner number almost invariably increased simultaneously, hence dilute hydrogen peroxide at the temperature of the water bath produced in chicken fat the same chemical change that occurs in that fat *in situ* during prolonged freezing.

Stearic and oleic acids were also oxidized with hydrogen peroxide. The saponification number of the acids decreased. This change is similar

¹ Results obtained in this laboratory and in course of preparation for publication.

² *J. Biol. Chem.*, 4, 77, 227 (1908).

³ Pennington, U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 115, 66.

⁴ *Ibid.*, *Bull.* 107, revised, 136-142.

TABLE III.—CHANGES IN THE CHEMICAL CONSTANTS OF CHICKEN FAT PRODUCED BY OXIDATION WITH HYDROGEN PEROXIDE.

Number of sample.	Description.	Iodine number.	Acid value.	Ester value.	Saponification number.	Hegner number.	Per cent. free acid as oleic.
Before Oxidation.							
360	Held in chillroom at 32° F. for 24 hours..	64.1	0.3	186.9	187.2	91.66	0.15
350	Western market chicken of known history...	66.7	2.2	195.9	198.1	95.20	1.11
2004-1A	Same as No. 350.....	64.5	1.7	186.3	188.0	90.76	0.86
2010-1A	".....	64.5	1.7	181.6	183.3	88.56	0.86
2010-1B	".....	64.9	1.0	179.7	180.7	88.14	0.50
2015-1B	".....	63.3	1.6	188.1	189.7	91.23	0.80
2018-1A	".....	73.7	1.6	183.2	184.8	89.99	0.80
343	Broiling chickens of known history, hard frozen for 12½ months.....	63.6	3.6	184.8	188.4	90.89	1.81
368	Oleic acid, C. P.....	62.8	193.7
369	Stearic acid, C. P.....	201.3
After Oxidation.							
360	Held in chillroom at 32° F. for 24 hours.....	64.6	0.5	198.9	199.4	95.95	0.25
350	Western market chicken of known history...	61.2	2.4	200.8	203.2	...	1.21.
2004-1A	Same as No. 350.....	53.1	4.1	205.5	209.6	91.14	2.06
2010-1A	".....	62.0	2.5	201.8	204.3	94.44	1.26
2010-1B	".....	66.9	1.8	198.8	200.6	96.16	0.91
2015-1B	".....	54.6	3.6	198.4	202.0	91.14	1.81
2018-1A	".....	61.6	3.6	202.8	206.4	91.79	1.81
343	Broiling chickens of known history, hard frozen for 12½ months.....	65.2	3.9	197.2	201.1	94.57	1.96
368	Oleic acid, C. P.....	64.1	192.0
369	Stearic acid, C. P.....	200.2

to that undergone by the fat of chickens kept hard frozen for a period of 4 months, at the end of which time both the saponification number and the Hehner number were lower than in the fat of fresh birds. For example, the fat of 12 chickens hard frozen for 4 months had a mean saponification number of 146.9 and a mean Hehner number of 66.27.¹

The fat of fresh chickens does not respond to the fuchsin-sulfurous acid test of Bianchi;² hence it may be assumed that compounds of the aldehyde-ketone family are absent. However, these compounds are present in the fat after oxidation with hydrogen peroxide, because a distinct pink or red color was produced by the oxidized fats when they were treated with fuchsin-sulfurous acid. Oxidized stearic acid also responded positively to the test. Oleic acid before oxidation gave a very faint pink, after oxidation a much deeper pink color. Crude fat from hard frozen chickens contains compounds which restore the color to fuchsin-sulfurous acid, as was shown by tests made on chickens hard frozen for periods of 22, 28, 29, 42, 54, 72, and 89 months. The aldehydes or ketones are usually insoluble in water, and only the fat is colored by the reagent. The biting, aldehyde-like odor of long preserved hard frozen chickens has been mentioned by Pennington.³

Dakin's work has shown that dilute hydrogen peroxide may oxidize saturated fatty acids with the formation of saturated fatty acids of lower carbon content, ketones, and occasionally aldehydes. In the course of this investigation it has been found that oxidation of chicken fat with hydrogen peroxide gives rise to a simultaneous increase in the Hehner number and the saponification number, while aldehydes are also formed. The increase in the saponification number is doubtless due to the formation of fatty acids which are homologues of those present in the unoxidized fat, but with a slightly lower carbon content. The increase in the Hehner number is explained by the formation of aldehydes and ketones. According to Browne⁴ aldehydes play a role in the determination of the saponification number and ester value of a fat in which they are present; during the saponification with boiling alcoholic potash, the aldehydes are partly changed into acids which neutralize a portion of the potash. But the rôle is a minor one, as shown by the ester value of oenanthol [*n*-heptyl aldehyde, $\text{CH}_3(\text{CH}_2)_6\text{CHO}$], which has been found to be 15.5. However, the formation of higher aldehydes and ketones, insoluble in water, increases the quantity of insoluble matter in the fat and, therefore, increases the Hehner number.

The changes in the fat of chickens during prolonged freezing are similar

¹ Pennington, *Premier Congrès International du Froid, Rapports et Communications*, 2, 252 (1908).

² *L'Orosi giornale d. Chem.*, 21, 253 (1898).

³ Yearbook, U. S. Department of Agriculture, p. 197 (1907).

⁴ *THIS JOURNAL*, 21, 975 (1899).

to the changes called forth by oxidation of the fat with hydrogen peroxide. The Hehner number and the saponification number increase simultaneously, and aldehydes are formed. The increase in saponification number may, therefore, be ascribed to the formation of slightly lower homologues of the fatty acids of fresh chicken fat, while the increase in Hehner number is doubtless due to the formation of aldehydes and ketones of high carbon content. These changes in the chicken fat *in situ* are probably produced by the action of enzymes.

During the earlier stages of keeping chickens hard frozen, a simultaneous decrease in both the saponification number and the Hehner number occurs; in explaining this phenomenon, both factors—formation of lower fatty acids and formation of ketones and aldehydes—again must be taken into consideration. The fat probably contains acids which, though insoluble in water, are on the border line between soluble and insoluble; these acids are converted into their lower homologues which are soluble; the Hehner number is thereby decreased, and a tendency is created to increase the saponification number. On the other hand, the higher acids of the fat are oxidized with the formation of aldehydes and ketones, and the saponification number is decreased, as happened in the oxidation of oleic and stearic acids with hydrogen peroxide; this oxidation tends to increase the Hehner number. However, as a resultant of these processes of oxidation, the Hehner number and the saponification number decrease simultaneously. In the course of prolonged freezing the chief role is played by the higher fatty acids, which are oxidized and give rise to an increase in both the saponification number and the Hehner number at the same time, as has been described.

NEW BOOKS.

Electro-Analysis. By EDGAR F. SMITH. Fifth Edition, Revised and Enlarged, with 46 Illustrations. Philadelphia: Blakiston's Son & Co. Price, \$2.50.

The fourth edition of this book was reviewed in *THIS JOURNAL*, 30, 477. The present edition contains, as new material, reviews of all the important work done on the subject during the past four years; also excellent descriptions of all up-to-date apparatus and methods. The book is to be highly recommended to those interested in electro-analysis.

It would seem advisable in works of this kind to give the size of the exposed electrode surface and the current in amperes or the surface and current density on the electrode in question, because the rate of deposition depends to a large degree on these factors. The voltage drop across the two electrodes depends upon a number of factors that may have little or no bearing on the efficiency of the method, *e. g.*, the distance of the electrodes apart, or the anodic polarization.

E. B. SPEAR.

Handbuch der Mineralchemie. Edited by DOBLTER, *et al.* Vol. I, Pt. 3, Bogen 21-30. Price, M. 6.50.

The latest issued pages of Mineralchemie continue the general subject of the carbonates. Calcium carbonate is concluded, and the carbonates of magnesium and calcium (dolomite), manganese, zinc, ferrous iron, cobalt, nickel, copper and strontium are considered. A few minor species like the hydrates of calcium carbonate are also included. We might raise the question whether it would not be more rational, in a work on mineral chemistry, to classify strontium carbonate with those of calcium and magnesium with which it *chemically* belongs, though in mineralogies it is put in another group. The mineralogies on crystallographic grounds also put aragonite in this later group, but here, fortunately, vital considerations have induced the editors to place aragonite with calcite. The work of Leitmeier, who has written the most of this heft, is especially good. His presentation of the synthetic work on aragonite is clear and logical, and the reader leaves it with a well-defined conception of its relation to calcite and of the prime factors which influence its formation. Coming then to the genesis of aragonite in nature, the author classifies its various occurrences in typical groups, pointing out as far as possible the significance of each in the light of synthetic work, though he does not hesitate to state that some are still inexplicable. The data relating to aragonite are, to be sure, on the whole consistent and readily handled. In dolomite (calcium magnesium carbonate), however, we have a mineral about the formation of which very little is known. Its geological importance has made it the subject of a large amount of investigation though, simple as it is, its synthesis has not been accomplished with certainty. It must have been a thankless task to write a digest of this mass of experimental detail, but Leitmeier has done it with an excellent sense of the significance of experiments and their relative values. Very wisely, the minor species of carbonates are treated very briefly; some of them, with further knowledge, may drop out altogether. The analytical directions of Dittrich deserve a word of commendation. The methods are well known, but they are briefly and very clearly given here. E. T. ALLEN.

Grundzüge der Dispersoidchemie. BY PROF. DR. P. P. VON VEIMARN. Th. Steinkopff. Dresden. 1911. pp. 121. Price, M. 4.

"This little book is the result of a series of lectures delivered by the author in April, 1910, at the invitation of the Microbiological Society of the Imperial Institute of Experimental Medicine at St. Petersburg," the present publication being a translation by F. Kleemann from the author's manuscript. The book is divided into an introduction, four chapters, a conclusion, and two appendices. The subject matter is treated under the following headings: 1. The colloidal state as a general characteristic of matter. 2. The chief methods for obtaining any given crystallin

substance in any desired degree of dispersion. 3. The conditions governing the stability of suspensoids and suspensions. 4. The principal properties of suspensides and emulsoids of substances of high molecular weight.

The book is characterized by a very evident careful attention to arrangement and systematization of the subject matter, which enhances its value for the average reader and impresses him with the fact that colloid chemistry is gradually being reduced to a science. Most of the experimental illustrations employed are taken from the numerous and important investigations carried out by the author and his students within the last six years.

On page 37 the definition of "condensation pressure," as *equal to a certain concentration difference* rather than *proportional to it*, is open to criticism. Many chemists will also disagree with the author's rejection of the term "amorphous." Certainly his "proof" (see Appendix I), that certain finely divided substances must *necessarily* consist of submicroscopic crystals because they are transformed into visible crystals by shaking with a suitable solvent, will not be accepted without question. On the other hand he succeeds in making it very probable that in the case of many precipitates, the distinction between "amorphous" and "crystalline" is one of degree rather than of kind.

Altogether the book is a very readable one and bears less resemblance to a descriptive catalogue than do many of the recent treatises on the subject.

EDWARD W. WASHBURN.

THE JOURNAL

OF THE

American Chemical Society

NINETEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1911.

BY F. W. CLARKE.

Received January 22, 1912.

During the year 1911 a fair number of investigations relative to atomic weights appeared, some of them being of a fundamental character. The actual data obtained are, briefly, as follows:

Chlorine.—Burt and Gray¹ continued their research upon the density of hydrochloric acid, confirming their earlier conclusions. For the weight of a normal liter of the gas at 0°, 760 mm., and the latitude of London they give the following figures:

1.63977	1.63999	1.64016
1.63999	1.64049	1.64037
1.64007	1.63982	1.64030
	1.64009	
	Mean,	1.64011

Reduced to latitude 45° this mean becomes 1.63915, whence Cl = 35.460.

Chlorine and Potassium.—Since the time of Berzelius the analysis of potassium chlorate has been of fundamental importance in the determination of atomic weights. The data, however, were discordant, and not in harmony with recent investigations. Now, with all modern precautions, Staehler and Meyer² have reanalyzed the compound, with the subjoined results. Absolute weights are given.

¹ *Chem. News*, 103, 161, 170. Their former determinations appear in the report of this committee for 1909.

² *Z. anorg. Chem.*, 71, 368.

PRELIMINARY.

Weight KClO_3 .	Weight KCl .	Ratio.
12.38248	7.53218	1.643943
11.28213	6.86340	1.643811
12.22480	8.65366	1.643791
11.52268	7.00963	1.643835
12.44913	7.57331	1.643816
Mean of the last four,		1.643813

Hence $\text{KCl} = 74.5558$. The first experiment was rejected.

FINAL SERIES.

Weight KClO_3 .	Weight KCl .	Ratio.
10.26355	6.24370	1.643824
10.08261	6.13362	1.643826
10.03177	6.10269	1.643828
10.63651	6.47073	1.643786
12.05095	7.33096	1.643842
Mean,		1.643819

Hence, $\text{KCl} = 74.5551$. From this the authors deduce $\text{K} = 39.097$, and $\text{Cl} = 35.458$, values in accord with the results obtained by other methods.

Sodium.—Some interesting analyses of sodium chloride and bromide are due to Goldbaum.¹ The salts were electrolyzed with a mercury cathode and a weighed silver anode, and on the latter the halogen was fixed in weighable form. Omitting a preliminary series of analyses of the chloride, the following data, with vacuum corrections, are given:

SODIUM CHLORIDE.

Weight NaCl .	Weight Cl .	At. wt. Na .
1.02234	0.62014	22.997
1.02221	0.62006	22.997
2.43474	1.47692	22.996
1.46370	0.88789	22.995
0.56934	0.34534	22.999
1.00793	0.61141	22.995
1.06501	0.64600	22.999
2.16720	1.31460	22.997
2.75219	1.66939	22.999
0.92900	0.56349	23.000
1.83527	1.11324	22.998
Mean,		22.997

Computed with $\text{Cl} = 35.458$. If $\text{Na} = 23.00$, $\text{Cl} = 35.462$.

¹ THIS JOURNAL, 33, 35.

SODIUM BROMIDE.

Weight NaBr.	Weight Br.	At. wt. Na.
1.05343	0.81803	22.998
1.33360	1.03561	22.997
1.95652	1.51936	22.995
5.02976	3.90586	22.997
2.09332	1.62554	22.998
6.46697	5.02178	23.000
5.54733	4.30768	22.999
7.03901	5.46606	22.998

Mean, 22.998

Computed with Br = 79.92. If Na = 23.00, Br = 79.927.

Sulfur.—The ratio between nitrogen and sulfur has been determined by Burt and Usher,¹ through analyses of nitrogen sulfide, N₄S₄. The substance was decomposed by passing its vapor at a red heat over quartz wool in a quartz tube, and from the volume of nitrogen so liberated its weight was computed. The following abbreviated table gives the essential data:

Weight N ₄ S ₄ .	Weight N ₂ .	Ratio, N/S.
0.469455	0.142726	0.43685
0.442787	0.134627	0.43688
0.456326	0.138736	0.43684
0.470072	0.142919	0.43686
0.466918	0.141969	0.43690
0.491307	0.149380	0.43688
0.484307	0.147257	0.43690

Mean, 0.43687

Hence, if N = 14.009, S = 32.067. In short, the new ratio confirms the accepted values for both nitrogen and sulfur.

Calcium.—Richards and Hönigschmid² have analyzed calcium chloride, and confirmed their former determinations of the atomic weight of calcium. The ratio 2Ag : CaCl₂ was measured, by the usual Harvard methods, with the results given in the next table. Vacuum weights are stated, and the reductions are based upon Ag = 107.88 and Cl = 35.457.

Weight CaCl ₂ .	Weight Ag.	At. wt. Ca.
4.60350	8.94908	40.075
4.82401	9.37780	40.074
4.81846	9.36688	40.076
5.29799	10.29911	40.076
5.40550	10.50832	40.073
5.24539	10.19715	40.073
5.34110	10.38328	40.072

Mean, 40.074

Hence, Ca = 40.074. The earlier bromide analyses gave Ca = 40.070.

¹ *Proc. Roy. Soc.*, 85A, 82.

² *THIS JOURNAL*, 33, 28.

A very rough determination of the atomic weight of calcium is due to Oechsner de Coninck.¹ He ignited calcium formate, and in four experiments found values for CaO from 55.94–56.11. In one other experiment he dissolved calcium carbonate in hydrochloric acid, precipitated the lime as oxalate, and finally ignited the latter. The mean of his five discordant values is $\text{Ca} = 40.02$.

Cadmium.—In order to determine the atomic weight of cadmium, Perdue and Hulett² have analyzed the hydrated sulfate electrolytically. The salt was electrolyzed over mercury, in which the liberated cadmium dissolved. The water of the sulfate was also determined at temperatures between 670° and 700° . The data, with vacuum weights, are as follows:

PERCENTAGE OF WATER.		
Weight $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$.	Weight H_2O .	Per cent. H_2O .
6.32863	1.1856	18.734
6.72493	1.25986	18.734
6.87537	1.2886	18.742
5.65027	1.05822	18.729
6.81125	1.27557	18.727
7.34977	1.37703	18.736
7.74837	1.3572	18.727
7.8843	1.47713	18.734
6.6100	1.2480	18.730

Mean, 18.733

PER CENT. OF CADMIUM IN $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$.		
Weight sulfate.	Weight Cd.	Per cent. Cd.
7.90902	3.46335	43.790
9.07468	3.97434	43.796
7.32787	3.20936	43.796
6.48847	2.84186	43.799
5.11684	2.24157	43.808
8.02954	3.51755	43.807
5.08743	2.22827	43.799

Mean, 43.799

PER CENT. Cd IN CdSO_4 .		
Weight CdSO_4 .	Weight Cd.	Per cent. Cd.
5.14303	2.77196	53.897
5.46507	2.94566	53.898
5.58677	3.01076	53.891
5.53568	2.98276	53.883
6.29717	3.39295	53.880
6.40718	3.45255	53.887
5.37196	2.89457	53.883

Mean, 53.888

¹ *Compt. rend.*, 153, 1579.

² *J. Physic. Chem.*, 15, 147.

From these data, when $S = 32.07$ and $H = 1.008$, the authors deduce $Cd = 112.30$, a value lower than that generally accepted. These new determinations have been criticized by Richards,¹ who suggests that the cadmium sulfate possibly contained an excess of water in "solid solution." Hulett is continuing his research with other cadmium compounds, and therefore judgment may well be suspended until the new evidence is published.

Iron.—Atomic weight redetermined by Baxter, Thorvaldson and Cobb² from analyses of ferrous bromide. The figures obtained are as follows, with all corrections applied:

PRELIMINARY SERIES.

Weight FeBr ₂ .	Weight Ag.	At. wt. Fe.	Weight AgBr.	At. wt. Fe.
3.45339	3.45481	55.840	6.01358	55.853
3.04933	3.05055	55.840	5.31029	55.844
2.9007	2.9019	55.839
3.0873	3.0885	55.844
3.50278	3.50426	55.837	6.10033	55.831
4.05239	4.05404	55.840	7.05752	55.831
4.08516	4.08683	55.840
		Mean, 55.840		
			Mean, 55.840	

FINAL SERIES.

Weight FeBr ₂ .	Weight Ag.	At. wt. Fe.	Weight AgBr.	At. wt. Fe.
5.03555	5.03744	55.834	8.76950	55.837
6.06309	6.06557	55.840	10.55889	55.839
5.59258	5.59482	55.482	9.73974	55.834
5.89767	5.90014	55.838	10.27507	55.844
4.48546	4.48742	55.834
5.41562	5.41799	55.834	9.43171	55.830
6.50002	6.50277	55.837	11.31958	55.843
3.56564	3.56719	55.834	6.20987	55.829
5.32434	5.32642	55.844	9.27237	55.839
6.38845	6.39094	55.844	11.12536	55.842
6.37952	6.38213	55.840	11.10971	55.844
8.51818	14.83468	55.836
		Mean, 55.838		
			Mean, 55.838	

In a second paper Baxter and Thorvaldson³ give another series of determinations, like the foregoing, but starting with meteoric rather than terrestrial iron. The results obtained are essentially the same, as is shown by the subjoined figures.

¹ THIS JOURNAL, 33, 888.

² *Ibid.*, 33, 319.

³ *Ibid.*, 33, 337.

Weight FeBr ₂ .	Weight Ag.	At. wt. Fe.	Weight AgBr.	At. wt. Fe.
3.95460	3.95631	55.835	6.88720	55.831
4.66954	4.67177	55.825	8.13282	55.818
4.75335	4.75550	55.831	8.27855	55.824
6.95582	6.95854	55.844	12.11329	55.844
3.20762	3.20904	55.833	5.58632	55.830

Mean, 55.834

Mean, 55.829

The authors reject the second and third of these pairs of determinations, leaving to be accepted the means 55.837 and 55.835. The calculations are based upon $\text{Ag} = 107.88$ and $\text{Br} = 79.916$.

Tantalum.—The determinations of this atomic weight by Chapin and Smith¹ were made by the hydrolysis of the pentabromide. The weights given below are corrected to a vacuum. $\text{Br} = 79.92$.

Weight TaBr ₅ .	Weight Ta ₂ O ₅ .	At. wt. Ta.
0.86837	0.33117	181.68
1.50903	0.57570	181.80
1.56554	0.59718	181.75
1.23239	0.47030	181.91
1.31815	0.50295	181.85
1.31702	0.50244	181.80
1.20090	0.45830	181.91
1.04050	0.39688	181.74

Mean, 181.80

This value is higher than that previously found by Balke, 181.52, from similar analyses of tantalum pentachloride.

Selenium.—Kuzma and Krehlik² have redetermined the atomic weight of selenium by reduction of SeO_2 with SO_2 . Special precautions were taken to secure a perfect reduction, and to avoid losses or impurities. The essential figures are as follows:

Weight SeO ₂ .	Weight Se.	At. wt. Se.
0.44245	0.31523	79.290
0.61918	0.44122	79.338
1.39106	0.99109	79.292
0.66740	0.47544	79.257
0.65154	0.46414	79.255
0.96042	0.68417	79.253
1.21088	0.86256	79.243
0.75468	0.53760	79.249
0.38577	0.27486	79.302
1.51040	1.07594	79.249

Mean, 79.273

Reduced to a vacuum standard, $\text{Se} = 79.26$.

¹ THIS JOURNAL, 33, 1497.

² *Trans. Bohemian Acad. of Emperor Francis Joseph*, 19, No. 13 (1910). In Bohemian. I am indebted for the details to the kindness of Professor Brauner, at whose suggestion the work was done.

Tellurium.—Harcourt and Baker¹ have criticized the work of Flint² upon the supposed complexity of tellurium, and conclude that the portions of low atomic weight which Flint obtained were contaminated by some impurity. They suggest that the basic nitrate employed in Flint's determination probably contained tellurium trioxide. Repeating his process of fractionation, they used the fourth fraction for atomic weight determinations, with the results shown below. The bromide method of Baker was employed.

Weight Te.	Weight TeBr ₄ .	At. wt. Te.
0.87822	2.20103	127.55
0.59706	1.49640	127.55
0.69189	1.73442	127.53
0.62732	1.57254	127.53
0.58307	1.46162	127.53

Mean, 127.54

I am informed that Flint is continuing his investigation, so that the question at issue still remains open. The value now given by Harcourt and Baker agrees with that found by Baker and Bennett in 1907.

Uranium.—In three very short notices Oechsner de Coninck³ gives approximate determinations of the molecular weight of UO_2 . First, UO_2Cl_2 was reduced to UO_2 by heating in hydrogen. In mean, $\text{UO}_2 = 270.07$. Similar reductions of $\text{UO}_2 \cdot \text{H}_2\text{O}$ gave $\text{UO}_2 = 270.66$. Another series with $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ gave $\text{UO}_2 = 270.46$. The last value corresponds to $\text{U} = 238.46$.

Iridium.—Hoyermann⁴ has determined the atomic weight of iridium by reducing $(\text{NH}_4)_2\text{IrCl}_6$ in a stream of hydrogen. His figures are sub-joined, with deductions based upon $\text{H} = 1.008$, $\text{N} = 14.01$, and $\text{Cl} = 35.46$.

Weight chloride.	Weight Ir.	At. wt. Ir.
1.72348	0.77205	192.645
1.77984	0.77654	192.598
1.78837	0.78011	192.533
1.15161	0.50249	192.635
1.73794	0.75838	192.654

Mean, 192.613

Holmium.—The atomic weight of holmium has been determined by Holmberg,⁵ by the well known sulfate method. His syntheses are as follows:

¹ *Jour. Chem. Soc.*, 99, 1311.

² *Am. J. Sci.*, [4] 30, 209. Cited in this report for 1910.

³ *Compt. rend.*, 152, 711, 1179; 153, 63.

⁴ *Sitz. phys. med. Soz. Erlangen*, 42, 278

⁵ *Z. anorg. Chem.* 71, 226.

Weight Ho_2O_3 .	Weight $\text{Ho}_2(\text{SO}_4)_3$.	At. wt. Ho.
0.3467	0.5687	163.57
0.3400	0.5579	163.40.
0.3960	0.6496	163.55
0.7631	1.2524	163.31
0.6877	1.1286	163.33
0.5378	0.8822	163.55

Mean, 163.45

Argon.—Fischer and Froboese¹ have made numerous fractional distillations of liquid argon, and found its density as gas to be practically constant. The final result is $d. 19.94\text{--}19.95$, and $A = 39.9$.

Niton.—For the atomic weight of niton, the gaseous emanation of radium, Gray and Ramsay² give determinations ranging from 218–227. The mean is 223; but the value $\text{Nt} = 222.4$ is preferred.

Miscellaneous Notes.—Hinrichs³ has reconsidered all the evidence relative to the atomic weight of hydrogen, and concludes that $\text{H} = 1.00781$. In another paper⁴ he discusses the atomic weight of vanadium, which he places at 51 precisely. A brief note by Ter Gazarian⁵ defends his work on the density of PH_3 . C. Henry⁶ has considered the proper mode of calculating atomic weights. Relations between the atomic weights are studied by Loring,⁷ by Emerson⁸ and by Nicholson.⁹ Emerson's "helix chimica" is an arrangement of the elements on a spiral, while Nicholson develops a structural theory of their formation.

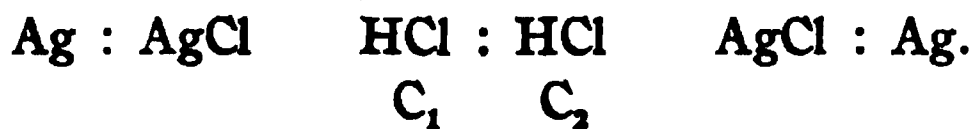
THE FREE ENERGY OF DILUTION OF HYDROCHLORIC ACID.

BY RICHARD C. TOLMAN AND ALFRED L. FERGUSON.

Received December 19, 1911.

I. Introduction.

The free energy of dilution of an electrolyte is usually obtained from measurements of the electromotive force of concentration cells. In the case of hydrochloric acid, apparently accurate measurements have been made by Jahn¹⁰ on concentration cells of the type,



¹ *Ber.*, 44, 92.

² *Proc. Roy. Soc.*, 84A, 536.

³ *Rev. gén. chim.*, 13, 351, 377 (1910).

⁴ *Proc. Am. Phil. Soc.*, 50, 191.

⁵ *J. chim. phys.*, 9, 100.

⁶ *C. R. Assoc. Franc. Avance Sci.*, 269 (1909).

⁷ *Phys. Z.*, 12, 107.

⁸ *Am. Chem. J.*, 45, 160 (1911).

⁹ *Phil. Mag.*, [6] 22, 864.

¹⁰ Jahn, *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900).

If E is the electromotive force of such a cell, then EF is the free energy change accompanying the passage of one faraday of electricity through the cell where F is the value of one faraday in coulombs. When one faraday passes, let us suppose that t mols of HCl are transferred from concentration C_1 to C_2 , then the free energy of dilution per mol of hydrochloric acid is evidently equal to EF/t .

An objection to this ordinary method of obtaining the free energy of dilution lies in the uncertainty as to the meaning and value of t . It is customary to use for t , t_{H} , the Hittorf transference number for hydrogen ion in hydrochloric acid, on the assumption that t_{H} will be the number of mols of HCl transferred from one electrode to the other when one faraday passes through the solution, and if the solution were of uniform concentration throughout the cell, this would, of course, be the case. In the actual measurement of electromotive force, however, a very small amount of current is allowed to pass, and this is accompanied by some complicated change at the boundary between the two concentrations of acid. It is open to doubt whether this change at the boundary is really equivalent per faraday to the transfer of t_{H} mols of hydrogen radical from C_1 to C_2 and $(1 - t_{\text{H}})$ mols of chloride radical in the opposite direction, as would be necessary if the total process including the electrode effects is to consist in the disappearance of t_{H} mols of HCl from the solution of concentration C_1 , and their appearance at concentration C_2 . The experimental fact,¹ that the potential difference between two liquids may vary with the time that they have stood in contact, certainly shows that for such cases the process accompanying the passage of electricity through the boundary is neither simple nor understood. In some cases a further uncertainty as to the value of t arises from the fact that the Hittorf transference number is different for solutions of different concentration. Moreover, in general, an exact determination of transference number is accompanied by very great experimental difficulties. Since there are these objections to the customary method of determining the free energy of dilution of an electrolyte, and since Jahn reached some rather extraordinary and much debated conclusions² from his measurements of electromotive force it seemed desirable to determine the free energy of dilution of hydrochloric acid without using cells with liquid boundaries. Such "concentration cells without transference" have been used or advocated by a number of investigators.³

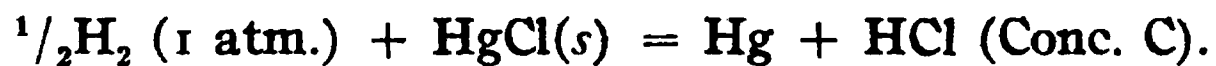
In this research, the electromotive force has been measured at 18° between calomel and hydrogen electrodes of cells containing hydrochloric

¹ Lewis and Rupert, *THIS JOURNAL*, 33, 299 (1911).

² Arrhenius, *Z. physik. Chem.*, 36, 28 (1901). Nernst, *Ibid.*, 36, 596 (1901).

³ Ostwald-Luther, "Physiko-chemische Messungen," p. 449 (1910). Leffeldt, "Electro-Chemistry," Pt. I, p. 211.

acid at a known concentration, C . This determines the free energy change ΔF_{18° of the reaction,



By making determinations with acid of different concentrations, it is obviously possible to calculate by subtraction the free energy of dilution of hydrochloric acid from one concentration to another.

2. Experimental Method.

The experiments were carried out in a thermostat at 18° in cells of the form shown diagrammatically in Fig. 1, which is drawn to scale, each cell containing as a check two hydrogen and two calomel electrodes.

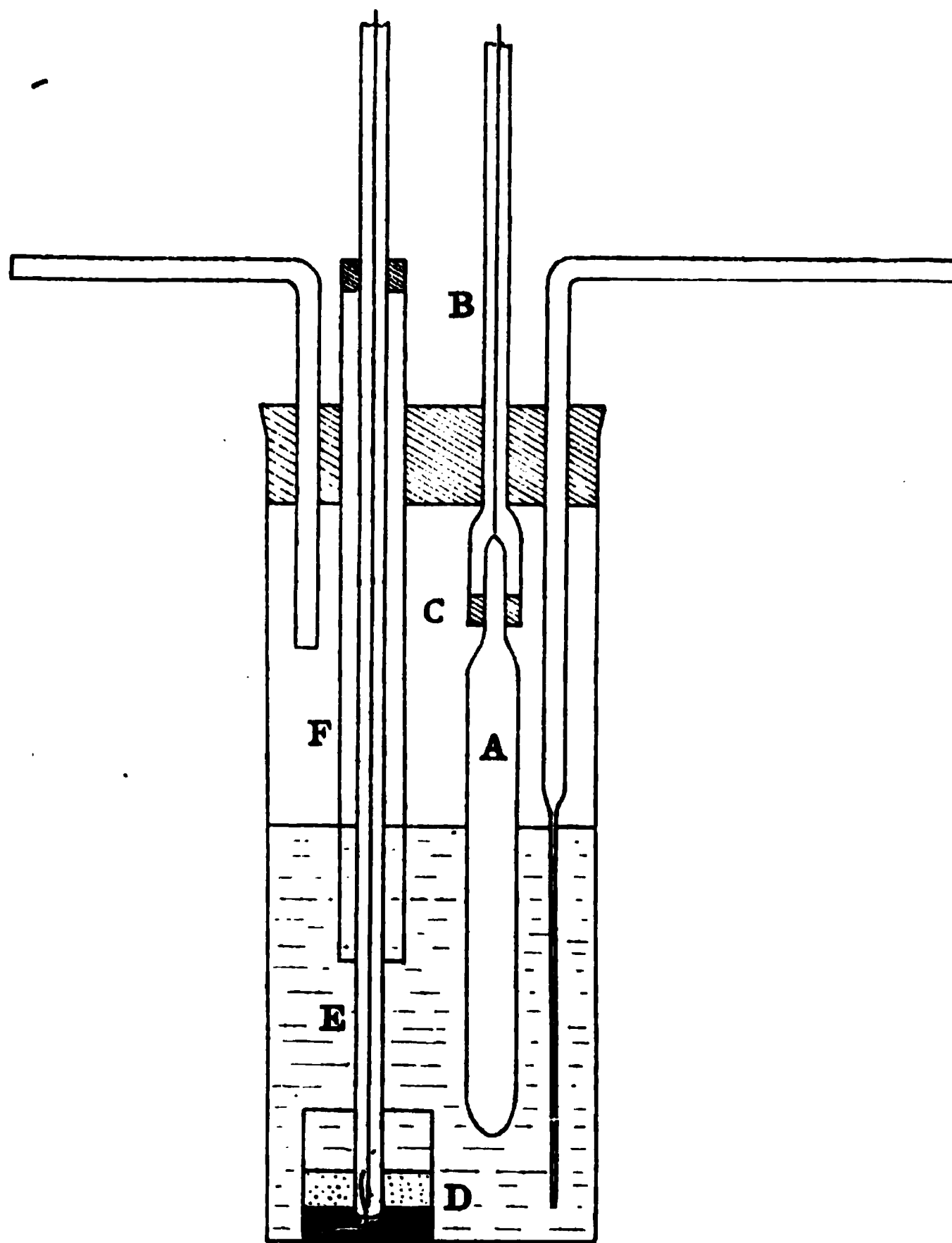


Fig. 1.

The Hydrogen Electrodes.—The hydrogen electrodes A were formed of a piece of glass tubing about 1 cm. in diameter sealed off at the lower end and drawn out above small enough to fit into the lower end of the

connecting tube B. They were fastened into the connecting tube by forcing them into the central hole in the small rubber stopper C. The electrodes A were previously covered with "Glanzplatin" (W. Heraeus) and then platinized (3 grams platinum chloride, 0.025 gram lead acetate, 100 cc. H_2O , drop in potential about four volts). Connection with the electrodes was made by pouring mercury into the tube B and inserting a copper wire.

In order to obtain electrodes of sufficient constancy, it was found necessary to replatinize them at frequent intervals (after one or two runs). The platinization was continued until the electrodes had a velvety black coating (15–45 minutes). After replatinizing, the pair of electrodes were placed for purposes of cleaning in a dilute solution of sulfuric acid and made alternately anode and cathode (drop in potential four volts), the current being commutated at minute intervals for a length of time depending on the length of platinization. This treatment was completed by the commutation of the current at five-second intervals during a period of several minutes. Before use the electrodes stood at least over night in distilled water and when not in use were kept in distilled water. These electrodes were perfectly reproducible and a number of them would not vary from each other by more than 0.02–0.03 millivolts in a day.

The Hydrogen Generator.—The hydrogen used was generated electrolytically from a strong caustic solution in a generator of the type described by Bodenstein.¹ The electrodes were of nickel wire.

In order to remove possible traces of oxygen, the gas was passed before use through a tube containing a platinum wire heated to incandescence by an electric current.² The stream was passed through a wash bottle filled with distilled water, then bubbled from a fine capillary through acid of the same concentration and temperature as that in the cell, and finally allowed to bubble from a fine capillary through the solution surrounding the platinized electrodes and escape through a tube into the air. After the cell had been in operation for a few hours it was found advantageous to change the flow of hydrogen so as to pass over the solution instead of bubbling through it, and this was uniformly done.³ The hydrogen entered the cell at a rate corresponding to about 40–50 bubbles, the size of a pea, per minute. When the two hydrogen electrodes in the same cell differed considerably from one another, it was sometimes possible to bring them together by shaking them or shaking the cell as a whole.

¹ Bodenstein and Pohl, *Z. Elektrochem.*, 11, 373 (1905).

² In general, however, when the current was shut off from the wire, the authors were able to detect no difference in the electromotive force.

³ Some very peculiar effects connected with the bubbling of hydrogen are now being investigated by one of the writers.

In general, when this was done attention has been called to the fact in the statement of the experimental results.

The Calomel Electrodes.—For the two calomel electrodes the materials were placed in small crystallizing dishes one inch in diameter by one inch deep (see Fig. 1, D). The electrodes for the whole series of measurements were prepared from the same batch of materials—redistilled mercury and Baker & Adamson's analyzed calomel serial No. 3772. New electrodes were prepared for each run on the day the run was started. Mercury and calomel were mixed together without grinding to form a paste with a little of the solution and then stirred with a larger amount of solution. In order to obtain constant electrodes, it was found necessary to use considerable depth of calomel especially in the more dilute solutions. Connection with the electrodes was made with the help of platinum wires sealed into a connecting tube (see Fig. 1, E) in which mercury and a copper connecting wire could be placed. The connecting tubes entered the cell inside the larger tubes F, to permit stirring without loss of hydrogen, which was found, however, to be unnecessary. Small potential differences were found between connecting tubes even when they dipped into the same mercury. This was specially noticeable if one of the platinum wires was cut off short. For use, connecting tubes were chosen which showed practically no potential difference (0.02–0.03 millivolts). The reproducibility of the calomel electrodes was nearly as good as that of the hydrogen electrodes.

The Electrical Apparatus.—The electromotive forces were measured with an Otto Wolff 15,000 ohm potentiometer and suitable galvanometer. A Weston cell No. 2041 was used as a standard and was kept in the same thermostat in which the measurements were carried out.

The Hydrochloric Acid.—An approximately fifth normal stock solution of hydrochloric acid was prepared by dilution with conductivity water from Baker & Adamson's analyzed hydrochloric acid C. P. and its concentration determined by precipitation of AgCl (five analyses, Cl, per 1000 grams solution 7.259, 7.265, 7.266, 7.262, 7.263).

The solutions used for measurement were 0.1 *N*, 0.02 *N*, 0.01 *N* and 0.002 *N* and were made from a weighed quantity of the stock solution by dilution at 18°, using one liter, 500 cc. and 100 cc. flasks. The flasks were carefully calibrated with standardized weights.

3. The Experimental Results.

Without a critical examination of the experimental data, it is impossible to judge of the value of a series of electromotive force measurements which pretend to more than superficial accuracy. The potentials of electrodes are always somewhat variable, and in the case of continuous-flow gas electrodes an additional complication is introduced by the possibility of a progressive change in the constitution of the solution.

TABLE I.

No.	Date.	Time.	Temp.	Bar.	0.1 N.		0.02 N.		0.01 N.		0.02N-0.1N.	0.01N-0.1N.
					A.	B.	A.	B.	A.	B.		
1	June 15	1.30 P.M.	39594	39600	47097	47059	50749	50775
2		3.00	18.1	733.1	628	628	7152	7160	658	658
3		4.00	18.1	33.1	633	641	7164	7176	634	638
4		5.00	18.0	33.1	632	642	7151	7147	614	616
5		6.30	18.0	33.1	643	650	7140	7133	604	605
6		8.00	18.1	33.1	611	608	7116	7000	579	578
7		9.00	18.0	33.3	603	608	7095	7090	566	570
8		10.00	18.1	33.5	600	610	7089	7090	562	564
9	June 16	9.00 A.M.	18.1	33.5	574	585	7010	7040	521	511	7445	10938
10		10.00	18.0	33.5	577	590	7001	7032	518	513	33	34
11		11.00	18.0	33.5	579	593	7000	7039	519	519	34	33
12		11.30	573	573	7010	7022	515	505	43	37
13		12.00	18.0	33.5	578	579	7011	7012	516	506	33	32
14		1.00 P.M.	18.0	33.5	577	583	7013	7030	520	507	45	37
15		2.00	577	577	7013	7030	512	510	45	34
16		3.00	18.1	33.1	585	582	6994	7003	522	521	15	38
17		4.30	18.1	578	589	7000	7013	526	518	23	38
18		6.00	18.0	33.1	577	578	7039	7048	512	506	66	31
19		9.30	18.0	34.5	590	590	7036	7079	509	508	68	19
20	June 17	8.00 A.M.	18.0	33.5	588	591	6997	7040	515	506	29	21
21		5.00 P.M.	18.0	33.4	574	586	6984	7026	505	499	25	22
22		9.30	18.0	33.8	558	577	6986	7023	501	499	37	32
23	June 18	9.30 A.M.	17.9	36.2	560	558	6989	7009	469	465	40	08
24		9.30 P.M.	18.0	36.2	596	598	6994	7036	508	502	18	08
Average,											7437	10930

Remarks:

Cell started June 15, 12 M.
Hydrogen changed to flow over the solution at 6.30 P.M.
Observation No. 11, cell containing 0.01 N solution was shaken after the reading had been taken.
Observation No. 14, upon shaking, the reading, B, in 0.1 N solution became 39577.
Observation No. 16, all the cells were shaken after the reading was taken.

TABLE II.

No.	Date.	Time.	Temp.	Bar.	0.1 N.		0.02 N.		0.01 N.		0.02N-0.1N.	0.01N-0.1N.
					A.	B.	A.	B.	A.	B.		
1	June 19	4.30 P.M.	18.0	735.4	39630	39622	47332	47326	50687	50634
2		5.00	18.0	35.4	619	613	270	263	620	606
3		5.45	18.1	35.4	613	611	243	243	600	588
4		8.00	17.9	35.6	585	587	214	213	521	519
5		10.00	18.0	36.0	580	583	208	207	504	509
6	June 20	9.00 A.M.	18.1	36.7	564	557	177	171	467	471	7613	10908
7		10.00	18.0	36.7	563	561	174	175	459	465	13	900
8		11.00	18.0	36.8	562	562	169	174	455	461	10	896
9		12.00	17.9	36.8	562	562	169	174	454	460	10	95
10		1.00 P.M.	18.1	36.8	553	560	167	174	453	451	14	95
11		3.00	17.9	36.8	550	556	160	164	448	436	09	89
12		4.00	17.1	36.4	554	555	152	168	446	439	05	88
13		5.30	18.1	36.4	565	565	158	174	465	451	01	93
14		8.45	18.3	38.5	563	574	165	183	471	455
15	June 21	8.30 A.M.	19.1	40.8	603	600	195	219	520	536
16		9.30	18.0	40.8	559	569	160	166	454	456	7599	91
17		10.30	18.0	40.6	556	570	161	168	459	460	7602	97
18		12.00	18.0	40.0	556	562	148	169	460	457	00	900
19		1.00 P.M.	18.0	39.6	553	563	163	167	456	448	07	894
20		2.30	18.0	39.5	553	566	167	173	458	437	10	88
21		3.30	18.0	38.9	566	566	169	169	456	456	03	90
Remarks:											Average, 7607	10895

Cell started June 19, 2.30 P.M.

Hydrogen changed to flow over the solution at 4.30 P.M.

Observations No. 14 and No. 15, these values were omitted from the calculations, owing to the poor temperature regulation.

Observation No. 17, the hydrogen electrodes in 0.1 N solution were shaken after the reading and then gave the values 39546 and 39547; ten minutes later they gave the values 39554, 39554.

Observation No. 18, the hydrogen electrode, A, in the 0.02 N solution was shaken, changing the readings to 47160, 47160.

Observation No. 20, 0.01 N solution was shaken at 3.00 P.M.

TABLE III.

No.	Date.	Time.	Temp.	Bar.	0.1 N.		0.02 N.		0.002 N.	
					A.	B.	A.	B.	A.	B.
1	June 21	10.30 P.M.	39595	39605	(47218)	47283	59200	58990
2	June 22	9.00 A.M.	18.2	738.4	567	555	(162)	170	58400	57752
3		10.15	18.	532	547	(137)	151	8330	7800
4		11.00	18.1	37.5	542	548	(119)	161	8310	7800
5		12.00	18.2	37.0	551	553	(139)	173
6		1.30 P.M.	18.1	36.6	552	549	(143)	167	8270	7800
7		2.30	18.1	36.4	527	536	(105)	172
8		3.30	18.1	35.7	540	550	(142)	174
9		5.00	18.0	35.4	540	550	(133)	160	8290	7851
10		8.30	18.1	35.9	551	555	(129)	156	250	877
11		9.30	18.0	35.9	551	559	(124)	166	270	865
12	June 23	8.00 A.M.	18.0	35.9	555	547	(160)	168	280	960
13		9.00	18.1	35.6	547	548	(120)	160	250	935
14		10.00	18.0	35.4	552	554	(126)	155	235	915
15		12.00	18.0	35.0	552	555	(112)	156	245	923
16		1.00 P.M.	18.0	34.5	555	555	(115)	154	215	92
17		2.00	17.9	34.3	549	552	(123)	156	220	91
18		3.00	17.9	34.4	556	556	(118)	145	220	93
19		5.30	18.0	34.4	556	555	(112)	156	220	923
20		8.45	18.0	35.3	558	552	(114)	155	235	950
21		10.30	18.1	35.3	556	551	(112)	142	150	955
22	June 24	8.30 A.M.	18.0	37.5	552	554	(153)	154	205	940
23		9.30	18.0	552	556	(150)	156	200	940
Remarks:					Average, 7609		18520			

TABLE IV.

No.	Date.	Time.	Temp.	Bar.	0.1 N.		0.02 N.		0.002 N.		0.002N-0.1N.	0.002N-0.1N.
					A.	B.	A.	B.	A.	B.		
1	June 26	8.15 P.M.	39630	39625	47338	47344	59085	59305
2	June 27	9.00 A.M.	18.1	732.6	553	560	212	227	8450	8475	7663	18906
3		10.00	18.0	32.6	569	572	217	233	453	470	54	891
4		11.00	18.0	32.6	562	575	213	225	430	453	50	73
5		12.00	18.0	32.6	575	585	217	225	442	465	41	74
6		1.00 P.M.	18.0	32.8	581	593	221	231	447	471	39	72
7		2.00	18.0	32.8	578	589	221	229	413	440	41	43
8		3.00	18.0	32.8	553	552	197	197	427	436	44	79
9		5.00	18.0	32.8	564	569	188	190	416	445	22	64
10		7.30	17.9	32.8	556	562	188	189	417	427	30	63
11		10.45	18.0	585	587	210	220	428	449	21	53
12	June 28	8.30 A.M.	17.9	37.5	574	571	202	206	428	424	31	53
13		10.00	18.0	37.5	576	578	213	217	435	452	38	67
14		11.00	18.0	37.5	584	58.	208	207	420	443	24	48
15		12.00	18.0	37.5	587	585	203	206	420	448	20	49
16		1.00 P.M.	18.0	37.5	586	591	210	211	418	451	22	45
17		2.00	17.9	37.5	584	583	204	205	412	447	19	44
18		3.00	18.0	37.7	58	594	209	217	422	453	22	47
19		4.00	18.0	37.9	595	59	215	-28	430	464	25	50
20		5.00	18.0	38.1	592	513	210	214	430	455	17	48
21		10.00	17.9	39.2	596	607	224	215	427	414	18	19
22	June 29	9.00 A.M.	18.0	41.5	609	611	239	240	439	475	30	47
Average, 7632											18859	

Remarks:

Cell started June 26, 5.00 P.M.

Hydrogen changed to flow over the solution at 8.30 P.M.

TABLE V.

No.	Date.	Time.	Temp.	Bar.	0.1 N.		0.02 N.		0.002 N.		0.002N-0.1N.	0.002N-0.1N.
					A.	B.	A.	B.	A.	B.		
1	June 29	5.30 P.M.	39671	39638	47390	47390	58920	58865
2		8.00	17.	741.0	635	620	290	282	556	500
3		9.30	18.0	41.0	623	614	269	261	493	450
4	June 30	8.30 A.M.	18.0	42.5	553	542	167	150	300	320	7611	18762
5		9.30	18.1	42.5	560	553	161	162	328	315	605	65
6		10.30	17.9	42.0	560	556	158	153	317	308	598	55
7		11.45	18.0	42.0	564	562	162	163	317	317	600	54
8		1.00 P.M.	18.1	41.5	561	547	178	170	326	329	20	74
9		2.00	18.1	41.5	565	543	184	174	327	327	25	73
10		3.00	18.0	41.0	560	573	188	176	320	323	15	55
11		5.00	18.0	40.6	559	571	185	171	305	315	13	45
12		11.15	18.0	40.0	553	573	190	180	316	320	22	55
13	July 1	10.00 A.M.	17.9	40.2	(535)	(408)	183	182	296	288
14		1.00 P.M.	18.1	39.1	563	(448)	194	190	300	295	29	35
15		2.30	18.0	38.9	567	(...)	195	191	315	270	26	26
16		4.00	18.0	38.4	561	(...)	199	195	305	290	36	37
17		10.00	18.1	38.4	560	(...)	200	180	320	295	30	48
Average, 7618											18753	

Remarks:

Cell started, June 29, 3.30 P.M.

Hydrogen changed to flow over the solution at 5.30 P.M.

Observation No. 13, before this observation the temperature had been very unsteady, just before the reading the 0.1 N cell had been shaken. These readings are omitted from the final average. Also, from this time on, all the readings on electrodes, B, 0.1 N solution, have been neglected on account of their abnormality.

In the preceding tables, I–V, are presented the experimental data from which our conclusions are drawn. These tables include all the measurements which were made at 18° , except one run in which the electrical connections were wrongly made so that the different cells electrolyzed each other.

It will be seen from the tables that measurements were made at the same time on three different cells containing solutions of different concentration. In the tables the first five columns give the number of the reading, the date and time when it was taken, the temperature of the thermostat and the height of the barometer. In column A for each cell is given the electromotive force in volts $\times 10^5$ between one hydrogen and one calomel electrode, and in column B the electromotive force between the other two electrodes. In all cases the calomel electrode was positive.

In each set of measurements cell No. 1 contained 0.1 *N* acid. The last two columns of each table give the difference between the average electromotive force in the 0.1 *N* acid and the average found for the two weaker acids. The electromotive force in any one cell is dependent on the barometric height, since that determines the pressure of the hydrogen supplied to the electrodes. If, however, the different cells respond equally quickly to changes in barometric height it is evident that the differences in electromotive force recorded in the last two columns should be independent of the barometric reading.¹ These differences multiplied by the value of Faraday's equivalent in coulombs give in joules the free energies of dilution of hydrochloric acid from tenth-normal concentration to the other dilutions.

As is to be expected, it will be seen from the tables that the electromotive forces are most reproducible in the more concentrated solutions. It will also be noticed that the electromotive force of the cells tends to fall pretty rapidly for several hours after the cell is set up and then usually remains reasonably constant for two or more days. In obtaining the final averages the writers have arbitrarily started with the readings obtained on the morning of the day after the cell was set up. Any readings omitted from the final averages are indicated in the notes accompanying the tables.

¹ Under favorable conditions, the authors have had no difficulty in observing the connection between barometric height and the electromotive force of the hydrogen electrode, the variations in electromotive force being of the calculated order of magnitude, but in general lagging somewhat behind the barometric changes. A further advantage of always measuring a cell containing 0.1 *N* acid along with the other concentrations lies in the practical elimination of errors, due to changes in the electromotive force of the standard cell. Any errors in the electromotive force of the standard cell produce an equal percentage error in each of the electromotive forces measured. Since these electromotive forces are, however, of the same order of magnitude the error from this source in their difference is negligible.

In the final averages it did not seem necessary to make any allowance for the fact that the readings were not taken at equal intervals of time.

It should be specially noticed that after the readings have become constant (*i. e.*, beginning with the day following the setting up of the cell), no systematic tendency appears for the electromotive forces to vary either upward or downward. In an extensive series of measurements which the authors had previously made at 25°, the electromotive forces showed a continued and decided tendency to decrease, especially in the more dilute solutions. In these earlier measurements, however, instead of changing the hydrogen so as to flow over the solution it was bubbled through the solution during the whole run. The cells were arranged, moreover, with the hydrogen and calomel electrodes in the separate arms of an H tube. The constancy of the measurements reported appears to be quite satisfactory.

Table VI summarizes the average values found in each set of measurements for the difference between the electromotive force in the 0.1 *N* solutions and the more dilute solutions. The final averages for all the sets of measurements are also presented together with the average deviation from the mean. Owing to the wide deviation, the bracketed value has been omitted entirely from the calculations. An examination of the table will afford an idea of the reproducibility of the measurements.

TABLE VI.—DIFFERENCES BETWEEN E. M. F. IN 0.1 *N* SOLUTION AND DILUTE SOLUTION.

0.02 <i>N</i> -0.1 <i>N</i> .	0.01 <i>N</i> -0.1 <i>N</i> .	0.002 <i>N</i> -0.1 <i>N</i> .
(0.07437)	0.10930	0.18520
0.07607	0.10895	0.18859
0.07609	0.18753
0.07632
0.07618
<hr/>	<hr/>	<hr/>
Average, 0.07617	0.10913	0.18711
±0.00009	±0.00018	±0.00127

The value in joules for the free energy of dilution, ΔF_{dil} , from 0.1 *N* to the more dilute solutions (of concentration *C'*) have been obtained by multiplying the final average differences in electromotive force by the value of Faraday's equivalent, 96580 coulombs. These values are represented in the second column of Table VII. The free energies of dilution are, of course, all negative.

4. The Fugacity of Hydrochloric Acid.

Accurate data on the free energy of dilution of an electrolyte are chiefly valuable for their bearing on the problem of ionic dissociation. Employing the well adapted conceptions introduced by Lewis¹ in his system

¹ Lewis, *Proc. Amer. Acad.*, 37, 49 (1901); *Ibid.*, 43, 259 (1907); *Z. physik. Chem.*, 38, 205 (1901); *Ibid.*, 61, 129 (1907). In the second of the above articles, Professor

of thermodynamic chemistry let us represent the fugacity of undissociated HCl in 0.1 *N* solution by the symbol f_{HCl} , and its fugacity in other concentrations under consideration by f'_{HCl} . Similarly, f_{H}^+ , f_{Cl}^- , $f_{\text{H}}'^+$ and $f_{\text{Cl}}'^-$ will represent the fugacities of the ions. If $\Delta F_{\text{dil.}}$ is the free energy change accompanying the transfer of one mol of hydrochloric acid from the 0.1 *N* solution to one of the more dilute solutions, we may write the following evident relation,

$$-\Delta F_{\text{dil.}} = RT \ln \frac{f_{\text{HCl}}}{f'_{\text{HCl}}} = RT \ln \frac{f_{\text{H}}^+ f_{\text{Cl}}^-}{f_{\text{H}}'^+ f_{\text{Cl}}'^-}.$$

Further, since C_{H}^+ , the concentration of hydrogen ion in any solution, is equal to C_{Cl}^- , the concentration of chloride ion, we may assume $f_{\text{H}}^+ = f_{\text{Cl}}^-$ and write

$$-\Delta F_{\text{dil.}} = 2RT \ln \frac{f_{\text{H}}^+}{f_{\text{H}}'^+}.$$

These "fugacity ratios" have been calculated from the free energy data; using the value *R* equals 8.3162 joules per degree, *T* equals 291.13°, and are given in columns four and six of Table VII. In these columns are also presented the deviations produced in the "fugacity ratios" by the average deviations from the mean electromotive forces given in Table VII.

TABLE VII.

<i>C'</i>	E. M. F.	$-\Delta F$	$f_{\text{HCl}}/f'_{\text{HCl}}$	$C_{\text{HCl}}/C'_{\text{HCl}}$	$f_{\text{H}}^+/f_{\text{H}}'^+$	$C_{\text{H}}^+/C'_{\text{H}}^+$
0.02 <i>N</i>	0.07617	7356.5	20.9 ± 0.1	7.76	4.57 ± 0.01	4.78
0.01 <i>N</i>	0.10913	1054.0	77.7 ± 0.3	17.3	8.82 ± 0.03	9.49
0.002 <i>N</i>	0.18711	1807.1	174.4 ± 9.1	112.5	41.8 ± 1.1	46.7

In general, it has been found for dilute solutions of non-electrolytes, and weak electrolytes, that the "active mass" or fugacity of the substances present is proportional to their concentration.¹ For this reason we have calculated from conductivity measurements, and presented in Table VII for comparison the ratios of the concentration of undissociated HCl in 0.1 *N* acid to that in the more dilute solutions, as well as the ratios of the concentration of hydrogen ion in 0.1 *N* solution to that in the more dilute solutions.

In calculating these concentration ratios, we have used the conductivity measurements of Kohlrausch² employing for Λ_0 the value 396 obtained

Lewis has definitely stated as a problem for research the determination of the relation between the concentration and fugacity (activity) of the components of an electrolytic solution. This article is a contribution to the quantitative solution of that problem. The fugacity of a substance and its activity, *a*, are connected by the equation $f = aRT$. Hence, the ratios for the fugacities of HCl and H^+ , given above, are the same as the corresponding activity ratios.

¹ See Lewis, THIS JOURNAL, 30, 673 (1908).

² Landolt and Börnstein.

from the work of Noyes and Sammet.¹ The ratio of the concentrations of the undissociated acid in the two solutions was calculated from the evident expression,

$$\frac{C_{\text{HCl}}}{C'_{\text{HCl}}} = \frac{\lambda_0 - \lambda}{\lambda_0 - \lambda'} \frac{n}{n'}$$

where λ and λ' are the equivalent conductances of the two solutions of normality n and n' . The ratio of hydrogen ion in the two solutions was calculated from the equation,

$$\frac{C_{\text{H}}^+}{C_{\text{H}}'^+} = \frac{\lambda}{\lambda'} \frac{n}{n'}$$

Referring now to Table VII, we notice wide discrepancies between the fugacity ratios and the concentration ratios of the undissociated acid as well as smaller but real differences between these ratios for the ions.²

If we assume that calculations from conductivity measurements give true values for the degree of dissociation of a "strong" electrolyte, we can not further explain these discrepancies exhibited by the ratios in Table VII, but must merely state that for "strong" electrolytes, *even in dilute solutions*, the fugacity of the ions is not strictly proportional to their concentration, while the fugacity of the undissociated electrolyte is very far from proportional to its concentration.

The remarkable nature of this result, however, may well be emphasized, since for all ordinary solutions, including even those of "weak" electrolytes, fugacity and concentration have been found closely proportional over wide ranges of concentration.³ In fact, this apparent deviation, for solutions of "strong" electrolytes from the laws obeyed by all other solutions, must cause us to regard with great suspicion the calculation of ionic concentration from conductivity measurements in the usual manner. Such calculations assume in general that the ions move with

¹ Noyes and Sammet, *THIS JOURNAL*, 24, 944 (1902).

² Before doing this work at 18°, the authors carried out an extensive series of measurements at 25° with solutions of concentrations 0.2, 0.1, 0.02, 0.01 *N*. These measurements were made in cells less well adapted to the purpose than the ones described above and the electromotive forces measured were more variable. Nevertheless, the computations led in every instance to similar differences between the fugacity and concentration ratios. Jahn, using KCl, NaCl and HCl solutions, also obtained similar differences for the ions between the concentration ratios as calculated from conductivity and electromotive force measurements. His data might also have been employed for calculating the fugacity ratios for the undissociated part of the electrolyte. A result of this nature was to be expected because of the well known deviations from the Ostwald dilution law shown by strong electrolytes when their degree of dissociation is calculated from conductivity measurements. That the discrepancies for the ions should be less than for the undissociated part of the electrolyte is to be expected from the approximate validity of the principle of solubility product. See also Lewis, *loc. cit.* For other examples of such deviations see Lewis and von Ende, *THIS JOURNAL*, 32, 737 (1910). Bray and MacKay, *THIS JOURNAL*, 32, 930 (1910); 32, 1213 (1910).

³ Lewis, *THIS JOURNAL*, 30, 668 (1903).

the same velocity under unit potential gradient in solutions of all different concentrations. The validity of this assumption was denied by Jahn,¹ who explained his results by assuming increased speed with increased concentration. It is greatly to be hoped that further investigation will throw light upon the actual facts.

In later articles one of the authors will present a method of calculating relative degrees of ionization from conductivity and transference data without assuming that the ions move with the same velocity at different dilutions.² Methods will also be presented of calculating the free energy of dilution from freezing-point and vapor-pressure data.

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI, OHIO, AND ANN ARBOR, MICH.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMAL DISSOCIATION OF BARIUM PEROXIDE.

By JOEL H. HILDEBRAND.

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Introduction.

The equilibrium between barium oxide, peroxide and oxygen has a technical interest due to the use of barium peroxide in the preparation of hydrogen peroxide, and in the historic, though now almost abandoned, Bria process for oxygen. It must also share in the general interest given to all heterogenous equilibria by the discussion of the applicability to them of Nernst's heat theorem.³ In addition to the researches of Bous-singault and others on this equilibrium we have the measurements of Le Chatelier⁴ of the dissociation pressures between 525° and 790°. In view of the discrepancies between later work and that of Le Chatelier, and the desirability of exact knowledge of this equilibrium, the following work was undertaken. Since its completion the writer has discovered a thesis by Wilhelm Becker, "Zur Frage der Erdalkaliperoxydbildung,"⁵ to which reference will be made in the discussion of the results of this work.

Apparatus.

The accuracy of measurements of this sort depends greatly upon the accuracy with which the temperature can be maintained and measured.

¹ See note, p. 245.

² The possibility of combining transference and conductivity measurements for calculating the degree of dissociation of electrolytes was suggested to the writer by Professor Lewis.

³ Foote and Smith, *THIS JOURNAL*, 30, 1344. Walden, *Ibid.*, 1350. Johnston, *Ibid.*, 1357.

⁴ *Compt. rend.*, 115, 655 (1892).

⁵ *Prag.*, 1909. (Work done at Karlsruhe.)

Every effort was made, therefore, to measure the temperature with unusual care. For this purpose a Pt, Pt-Rh thermocouple was used, made by Heraeus and calibrated just before use by the Bureau of Standards. From the data given by the Bureau the constants in the familiar quadratic formula were calculated connecting temperature and e. m. f. The e. m. f. of the couple was determined by the aid of a Wolff potentiometer, a Leeds and Northrup "Type H" galvanometer, and a Weston cell, standardized by the Bureau of Standards. The constant potential was obtained from two large cells as described by Hulett.¹ The accuracy of this combination was tested further by determining the melting point of pure zinc. The e. m. f. at which the zinc solidified gave, by use of the formula for the couple, the true value, 419° . Any errors in the values for temperature given later can hardly be due to the method of measurement, but must be ascribed to the difficulty of maintaining high temperatures constant within one or two degrees. For the experiments in which precision was not required the temperature was determined by means of a Siemens-Halske galvanometer, the scale of which was corrected by use of the values obtained with the potentiometer. In all the precision work the cold junction was maintained at 0° by immersion in cracked ice.

The peroxide was heated in an electric furnace made by winding on a porcelain tube, 2.2×30 cm., two layers of "Nichrome" ribbon, $\frac{1}{16}$ inch wide and 0.0035 inch thick. The layers had resistances of 70 and 90 ohms, respectively. They were insulated from each other and protected from the tube by asbestos paper and a paste made of water glass and magnesia. The whole was packed with broken pipe covering into an earthenware pipe and the ends fastened with asbestos board and the water glass paste. The two coils could be connected either separately, in series, or in parallel, an arrangement permitting great variations in temperature without requiring a regulating rheostat of great capacity or the undue waste of current. A temperature of over 1000° was easily obtained with this furnace. To insure uniform temperature in the middle third of the tube, not only was the ribbon wound more closely at the ends than at the middle, but a copper tube 12 cm. long, and covered with water glass to prevent oxidation, was placed within the porcelain tube of the furnace. When the ends of this copper tube were plugged with asbestos the temperature was constant within one degree throughout the interior. The current heating the furnace was controlled by means of a rheostat and ammeter.

In order that the equilibrium pressures might be attained rapidly, the space to be filled by the evolved oxygen was made as small as possible, not only in the tube containing the peroxide, but in the manometer

¹ *Phys. Rev.*, 27, 33 (1908).

as well. The tubes used differed slightly in the different experiments so they will be described as the experiments are taken up in detail. The manometer was arranged so that mercury could either be poured in from a pipet at the top of the open arm or run out at the bottom through a stopcock, thereby making it possible to keep the mercury at approximately the same height in the arm leading to the tube containing the peroxide, in spite of changes of pressure in the latter. Moreover, immediately above the mercury the manometer tube narrowed to a capillary which led to the tube in the furnace and had a T-arm provided with a stopcock through which the apparatus was exhausted at the beginning of each experiment and oxygen could be removed later on. The open arm of the manometer was twice as long as the constant level arm, so that pressures could be measured between 0 and 2 atmospheres. The position of the mercury was measured on a scale clamped to the manometer, a sliding device being used to avoid parallax. Pressures could be read to within 0.2 mm., but the unavoidable temperature errors make such accuracy unnecessary.

A small but efficient home-made Antropoff pump¹ served for exhausting the apparatus and removing oxygen.

Material Used.

The barium peroxide used was prepared from "C. P." barium hydroxide. The latter was recrystallized and freed from carbonate, dissolved in cold water and treated with successive portions of hydrogen peroxide, precipitating hydrated barium peroxide. The first precipitate was rejected, the middle fraction being filtered, washed, pressed dry, and put at once into a desiccator over phosphorus pentoxide which was then evacuated. It was left thus for two weeks, during which time all but a trace of the water was removed, leaving the anhydrous peroxide. A portion of this material was tested with the spectroscope. No calcium or strontium could be detected.

Investigation of the Nature of the Phases.

Several preliminary measurements of pressure-temperature curves gave different values of pressure at the same temperature in the different experiments, showing the system to be divariant, which proved that, since there were two components, only two phases could be present, indicating that the barium oxide resulting from the decomposition of part of the peroxide did not, at least at first, appear as a new phase, but must form a solid solution with the excess of peroxide. This important fact is merely mentioned by Le Chatelier, no details being given. It seems to have escaped the notice, therefore, of even the most detailed text-books.

¹ *Chem. Ztg.*, 34, 979 (1910).

In order to investigate the phase relations of the system, a study was made of the effect upon the pressure of removing successive portions of oxygen, the temperature being held constant. For this purpose a pipet-shaped vessel with a volume of about 20 cc. was made of Jena glass, the bulb filled with 0.708 g. of BaO_2 , and a closed Jena tube slipped into the larger outlet of the "pipet." Into the larger tube of the "pipet" was inserted a slightly smaller one, closed at the inner end which was pushed into the middle of the charge and cemented to the "pipet" at the outer end with marine glue. This tube served as the protecting sheath into which the thermocouple was placed, the wires being insulated from each other by Jena tubing 1 mm. in diameter. The charged "pipet" was placed in the electric furnace and the smaller tube leading from the bulb was cemented to the manometer with marine glue. The ends of the electric furnace tube were plugged with asbestos as far in as the ends of the bulb of the "pipet."

The apparatus was exhausted to less than 1 mm. at 200° . The temperature was then raised to 750° and oxygen was removed in successive portions, collected in a eudiometer over mercury at the outlet of the pump, the volume, temperature, and pressure of the oxygen in the eudiometer, and the pressure of that in the "pipet" in the furnace being noted after each removal. The volume of oxygen removed was reduced to standard conditions, and the pressure corrected by frequent readings of the barometer, the proper temperature corrections being made in each case.

TABLE I.

I. $t = 750^\circ$.		II. $t = 794^\circ$.		III. $t = 710^\circ$.		IV. $t = 710^\circ$.		V. $t = 695^\circ$.	
v.	p.	v.	p.	v.	p.	v.	p.	v.	p.
5.3	783	23.0	797	6.8	659	14.4	790	47.5	940
8.0	635	24.0	730	7.3	508	16.5	510	50.0	560
12.4	423	29.6	483	8.5	375	19.5	350	53.0	108
19.6	282	31.5	485	9.6	275	21.5	145	53.7	90
30.6	261	47.2	477	10.6	190	25.0	123	54.3	90
38.2	252	53.0	475	12.2	114	26.2	118	58.8	0
39.6	250	54.6	475	13.6	113	31.5	112		
47.4	250	58.0	430	16.2	110	34.0	112		
53.3	248	58.8	315	22.4	108	36.3	100		
59.2	250	60.1	197	28.1	102	37.7	104		
61.4	92	60.9	69			39.7	101		
63.3	35	62.1	0			42.4	104		
64.1	0					51.4	117		
						53.9	118		
						55.8	111		
						60.3	0		

The results are given in Table I and plotted in Curve I in Fig. 1. The higher pressures have no quantitative significance in this case because

the volume of the "pipet," manometer, and connecting tubes was not known, hence it was impossible to calculate how much oxygen had been removed from the barium peroxide but still remained in the apparatus.

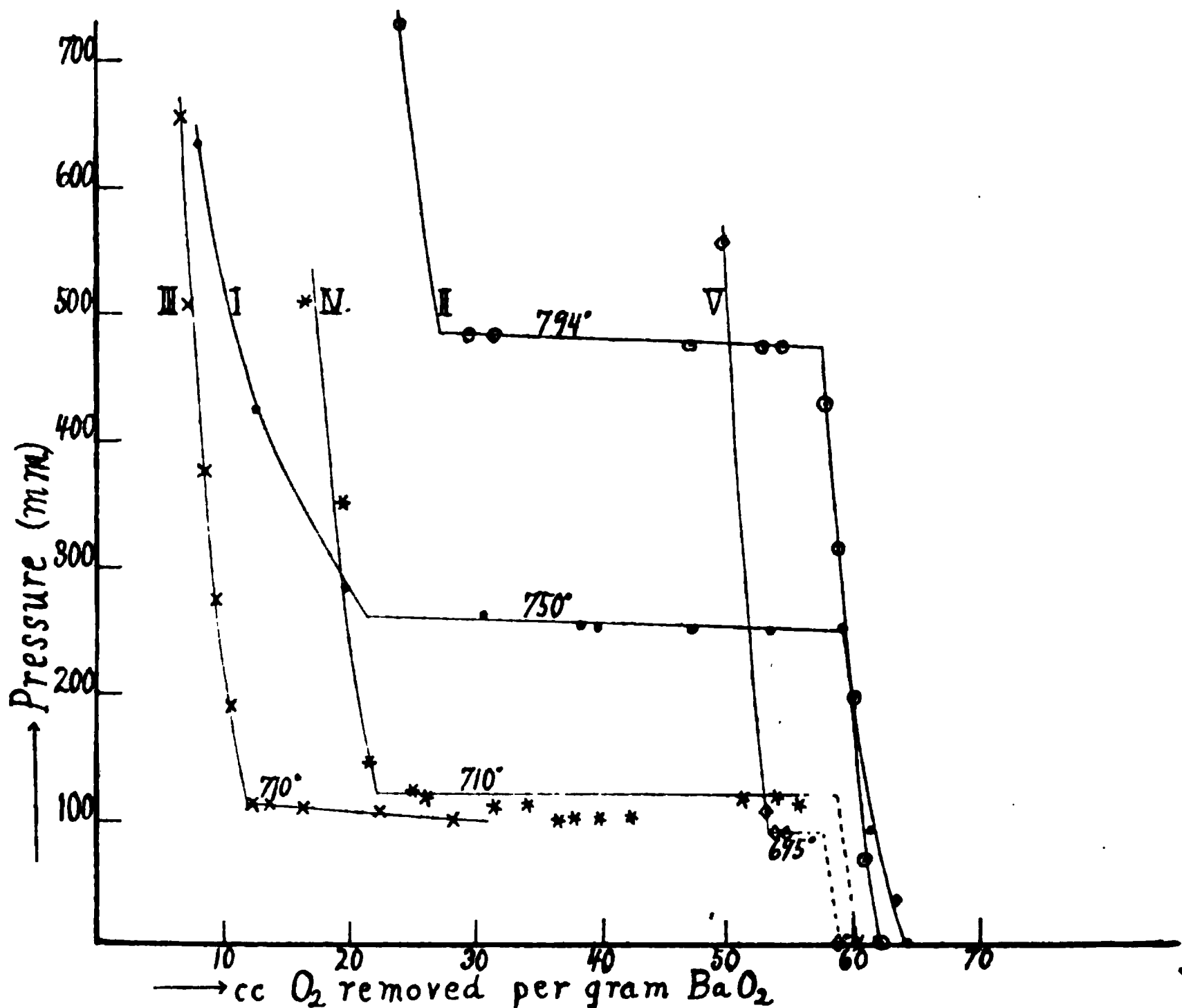


Fig. 1.

The results show quite clearly, however, that the system is divariant until about one-third of the peroxide has been decomposed, and then univariant till about 92% has been decomposed, and then divariant again. It is thus quite evident, in the light of the phase rule, that there can exist two solid solutions, one of barium oxide in peroxide, and another of peroxide in oxide, and that the usual pressure-temperature curve has a definite significance only in the region where these two solid solutions are saturated and coexistent. In the univariant system equilibrium is reached very rapidly; in the divariant system more slowly, since diffusion in the solid must take place till a new concentration is reached.

In order to ascertain more accurately the limits of the univariant system, containing tubes were made having as little volume as possible in excess of that occupied by the peroxide. The values given in Column II were obtained using a quartz tube as shown in Fig. 2. The end was blown into a bulb in an oxy-gas flame. The inner tube, protecting the

couple, fitted snugly within the outer, connection being made between the latter and the manometer by means of the T-tube shown on the figure. The parts were cemented together by means of marine glue. A



Fig. 2.

fine quartz tube insulated the wires of the thermocouple from each other (not shown in the figure). The bulb was packed tightly with 1.415 grams of barium peroxide in this experiment. When set up as described the free space in the tube was determined by collecting and measuring the air removed in the process of exhaustion. This was found to be 3.54 cc. The values given for "cc. of O_2 removed," in this and subsequent experiments, include the oxygen remaining in the apparatus, and thus represent the amount of oxygen removed, not from the apparatus, but from the peroxide. Since the charge contracts as it decomposes, and since the oxygen in the above free space of 3.54 cc. is not all at the same temperature, the correction is not very accurate, as a mean temperature had to be selected rather arbitrarily in reducing the volume to 0° and 76 cm. Of course, at lower pressures the amount in the tube is small, so that the correction is then small. Experiments III and IV, where the free space is still smaller, and the pressure when the system begins to be univariant is low, are thus more accurate than this one. The temperature in Experiment II was kept constant at 794° . A slight drop in pressure is noticed in the middle portion of the curve where the pressure should apparently be constant. The reason for this becomes clear in the next two cases.

In Experiment III, carried out at 710° , the charge was placed in a Jena tube, the lower temperature not requiring quartz. A thick-walled bulb was blown on the end of a tube and filled with 2.029 g. of peroxide. Into the tube between the bulb and the end connected with the manometer was slipped a closely fitting rod of Jena glass to reduce the free space as much as possible. The thermocouple was introduced into the other end of the furnace, so that the junction was beside the bulb containing the peroxide. The free space in the tube was reduced to 2.5 cc. by this arrangement. The system became divariant when about 12 cc. of oxygen had escaped from 1 g. of peroxide. The pressure decreased slightly and the evolution of oxygen ceased after 28 cc. per g. of peroxide had been withdrawn. This is in accordance with the fact that a slight amount of water must be present as a catalyst in order for the reaction

to proceed. This behavior is reported by Le Chatelier and others, and is taken account of in the Brin process for oxygen, where the air used to regenerate the peroxide must not be completely dried, as the absorption will not then take place. This experiment having been performed two weeks later than the previous one, and the peroxide having remained in the desiccator in the interval, it contained less water, what there was being removed with the first portion of oxygen, leaving the charge too dry to react.

Experiment IV was carried out at the same temperature, 710° , the only difference being that a quartz tube was used instead of one of glass. The charge weighed 1.393 g., and the unoccupied volume was 2.5 cc. The results are shown in the table and curve. After the removal of 42.4 cc. of oxygen, the evolution ceased, as in the previous experiment. A few milligrams of water were admitted, whereupon the pressure rose slightly and the evolution of oxygen continued till 55.8 cc. were removed, after which, the water not having permeated the whole charge, the pressure fell and 60.3 cc. were obtained with difficulty.

In Experiment V the effect of a larger quantity of water is illustrated. The tube, of Jena glass, contained 1.019 g. of peroxide and 0.34 g. of water (of which much was driven out of the peroxide space before higher temperatures were reached). The free space was 1.2 cc. The temperature was 695° .

It is quite evident, from these results, that this equilibrium can be understood only by taking into account both the part played by the water present and the existence of solid solutions.

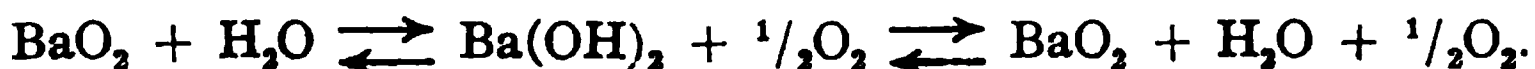
The presence of water introduces the equilibrium:



It seems likely¹ that the barium peroxide decomposes first into oxygen and hydroxide, thus:



and that the oxide is formed from the latter, regenerating water. The complete equilibrium might therefore be written thus:



In addition, the oxide and peroxide are soluble to a limited extent in each other. According to Johnston,² who measured the dissociation pressures of barium hydroxide at different temperatures the hydroxide and oxide seem to form no solid solutions with each other. It would seem unlikely, also, that the peroxide and hydroxide should form a solid solution, which is confirmed by the behavior of Curves III and IV, especially the latter. As the charge becomes dry the pressure falls about

¹ See Dissertation of Becker, pp. 28-32.

² *Z. physik. Chem.*, 62, 330 (1908).

20 cm., and then rises an equal amount upon the addition of a little water, and the consequent formation of hydroxide. Now Johnston gives the following values for the dissociation pressure of barium hydroxide:

$t^{\circ}\text{C}.$	670	749	829	910	998
p (mm. of Hg).....	17.4	55	149	355	760

Using the van't Hoff "reaction isochore" the pressure at 710° is calculated to be 28 mm., just a little more than the above drop as the material became dry, or as the hydroxide present was decomposed. The fall is not sudden as the amount of hydroxide present gradually becomes less and hence gradually less able to give off enough water vapor to exert the full equilibrium pressure. If equilibrium were attained the phase rule shows that when the following phases are present, gas (O_2 and H_2O), $\text{Ba}(\text{OH})_2$, and two saturated solid solutions of barium oxide and peroxide, each on the other, the system is univariant, and therefore can exert only one pressure for every temperature. At the beginning and end of the curve, when only one solid solution is present, the system possesses an additional degree of freedom, so that concentration must be fixed in order to fix the pressure. The different values shown by the curves at which the system becomes univariant are evidently due to initial differences in the water or barium hydroxide contained in the charge. The original hydrated peroxide, though spread out in the desiccator in as thin layers as possible, would hardly dry uniformly, and even in the cold decompose slightly according to the second equation given above. The mutual solubilities of the oxide and peroxide may also increase with the temperature, as comparison of Curve II with the others would seem to indicate. However, the difference between the saturation points of II and IV, at different temperatures, is less than the difference between III and IV, at the same temperature, so that the results give no very definite information on this point. The increase would seem to be not very great, which would be in accordance with the practically constant heat of reaction calculated later.

These results accord with and further explain those of Becker, and give additional information concerning the control of this reaction.

Becker passed oxygen under slightly more than one atmosphere pressure over barium oxide heated to a definite temperature in an electric oven. Successive equal samples were acted upon by the oxygen of definite moisture content for equal times and the product analyzed, the results showing the per cent. of peroxide formed at various temperatures. Among other results obtained by him the following are typical:

Temperature.....	200	300	350	400	500	600	700	750	800	850	900
% BaO_2 , using oxygen..	3.7	17.3	71.1	96.4	100	100	96.9	61.9	18.2	3.4	0.9
% BaO_2 , using air.....		18.2		70.4	69.2	52.8	30.9			5.9	

It is to be expected that the reaction will be incomplete at low temperatures on account of low velocity. The *gradual decrease* in the yield, however, for which Becker fails to account, can be explained only by the existence of a solid solution of peroxide in oxide, as otherwise the system would be univariant at the end, and as soon as the temperature had risen to a certain value the yield would fall at once to zero. A yield of 100 per cent. was obtained only at 600° and below, although the measurements of Le Chatelier would indicate this yield up to about 800° where, according to his measurements, given later, the dissociation pressure becomes one atmosphere. The curves here given, however, show that in order to obtain a yield of 100 per cent. not only must the pressure of the divariant system be kept below that of the oxygen used, but also that of the univariant combination represented by the sloping first part of the curve. Air at one atmosphere pressure is insufficient to give a yield of 100 per cent. in reasonable time because of the low velocity at the corresponding temperature. The partial pressure of the water vapor present must also be just a little less than the dissociation pressure of barium hydroxide in order that the oxide may not be converted into hydroxide instead of peroxide. Some is necessary, however, in order that the reaction may take place. Where the concentration of the barium oxide varies the aqueous concentration varies accordingly. These results show why 100 per cent. BaO_2 is not on the market and show what conditions must be fulfilled in order to obtain it.

In using this reaction for preparing oxygen from the air the first method was to allow air to pass over barium oxide heated to a dull red heat, forming peroxide. The retort containing the material was then raised to a much higher temperature whereby oxygen was driven off. The process worked in this manner was slow and costly, the alternate heating and cooling of the retorts requiring much time and fuel. The process was greatly improved by alternating the pressure instead of the temperature in order to reverse the reaction. This effected a great saving of time and fuel, as the reversal could be quickly effected, thus making many cycles possible where before only a few were obtained. However, according to the Brin Oxygen Company the quantity of oxygen obtained in each operation was only one-tenth of the amount calculated from the weight of barium oxide used. The data here presented make this low yield intelligible. The temperature was held at about 700° and the air, purified from carbon dioxide, dust, and part of its moisture, was forced over the barium oxide at a pressure of about three atmospheres, corresponding to a partial pressure of oxygen of about 450 mm. of mercury. Reference to the curves already given will show that this pressure is quite insufficient, at 700° , to convert all the oxide into peroxide, even with a minimum amount of hydroxide present. With any considerable

amount of hydroxide present the quantity of peroxide formed would be still less. The reverse operation would, according to the curves, be more nearly complete. Of course the yield would be still further reduced, in working the process on a large scale, by failure to obtain the true equilibrium.

The Pressure-Temperature Curve for the Univariant System.

Since the system is univariant for a considerable portion of the total range, provided that barium hydroxide is not present in too great quantity, a knowledge of the relation between temperature and pressure is of importance in this interval. This determination was made as part of the data secured from Experiment II, given above. The above experiment was interrupted after the removal of 47.2 cc. of oxygen and continued after the following data were secured, the interval requiring three hours. Equilibrium is attained quite rapidly in the univariant system, so that the time necessary for the experiment was consumed chiefly in waiting for the furnace to reach constant temperatures, and not in any lag of pressure. The temperature was measured as described above with the potentiometer, the e. m. f. being easily determined within 0.01 millivolt, which corresponded approximately to 1°. The results are given in Table II. The first column contains temperatures, the second the corresponding pressures in mm. of mercury at 0°. In the third column the heat of reaction is given calculated from one value to the next by means of the familiar formula of van't Hoff:

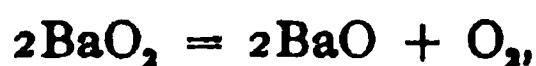
$$Q = \frac{4.571 T_1 T_2}{T_2 - T_1} \log p_2/p_1.$$

In the fourth column are given values of pressure calculated from the empirical equation,

$$\log p = -6850/T + 1.75 \log T + 3.807,$$

where p is expressed in mm. If p is expressed in atmospheres, the constant term becomes 0.926. The observed values, as is seen in the table, agree closely with those calculated from this equation.

Since it is probable that the partial pressure of the aqueous vapor present is not very different from that given in the dissociation of barium hydroxide alone,¹ the measurements of J. Johnston of that equilibrium, already given, enable one to calculate approximately the partial pressure of the oxygen in the equilibrium,



bearing in mind always the fact that the oxide and peroxide in the above

¹ In the present system the partial pressure of steam is probably slightly greater than from the hydroxide alone, as the resulting barium oxide has its concentration diminished by the dissolved peroxide.

equation are present in two saturated solutions of composition fairly constant. The fifth column in the table gives the values of aqueous pressure calculated by the van't Hoff equation to the temperatures of the present observations. The sixth column gives the partial pressure of oxygen found by subtracting the aqueous pressure just given from the smoothed values of total pressure given in column four. In the last column are given the heats of reaction calculated for the oxide equilibrium alone by using the partial pressures of oxygen. The mean value, 37420 cal., is in poor agreement with that given by Berthelot,¹ 24200 cal., even if proper allowance is made for the change of the reaction heat at constant pressure with the temperature, as it seems unlikely that the formation of solid solutions should give rise to such a large heat effect, and of the sign which would be indicated by the above difference. The formation of the solid solutions from the oxides is doubtless attended by an absorption of heat which is moreover not very great, since the solubilities appear to increase, and but slightly, with the temperature.

TABLE II.

Temperature.	Pressure (observed).	Heat of reaction (total).	Pressure (calculated).	Aqueous pressure.	Oxygen pressure.	Heat of reaction (2BaO + O ₂).
540	2	2.8
618	18	18.6	7.3	11.3
655	41	36500	40.5	13.7	26.8	38300
697	91	34000	91.7	26.3	65.4	38000
737	193	36500	188	47	141	36900
794	479	34200	476	98	378	36900
835	871	34300	877	159	718	36800
853	1128	35400	1132	195	937	36800
868	1401	36700	1397	231	1166	37000
	Mean,	35370			Mean,	37420

The results given in Table II are plotted in Fig. 3, along with the measurements of Le Chatelier which are as follows:

t.....	525	555	650	670	720	735	750	775	785	790
p.....	20	25	65	80	210	260	340	510	620	670

It will be seen that the pressures here given are lower than those of Le-Chatelier. His high pressures at 525° and 555° are surely incorrect.

Since the solid phases appear to be of nearly constant composition, it is interesting to note the order of agreement between these data and the equation given by Nernst² for the approximate calculation of heterogeneous equilibria,

$$\log p = -Q/4.571 T + 1.75 \log T + C,$$

¹ *Ann chim. phys.*, [5] 6, 209 (1875).

² "Thermodynamics and Chemistry," *Scribner's*, 1907.

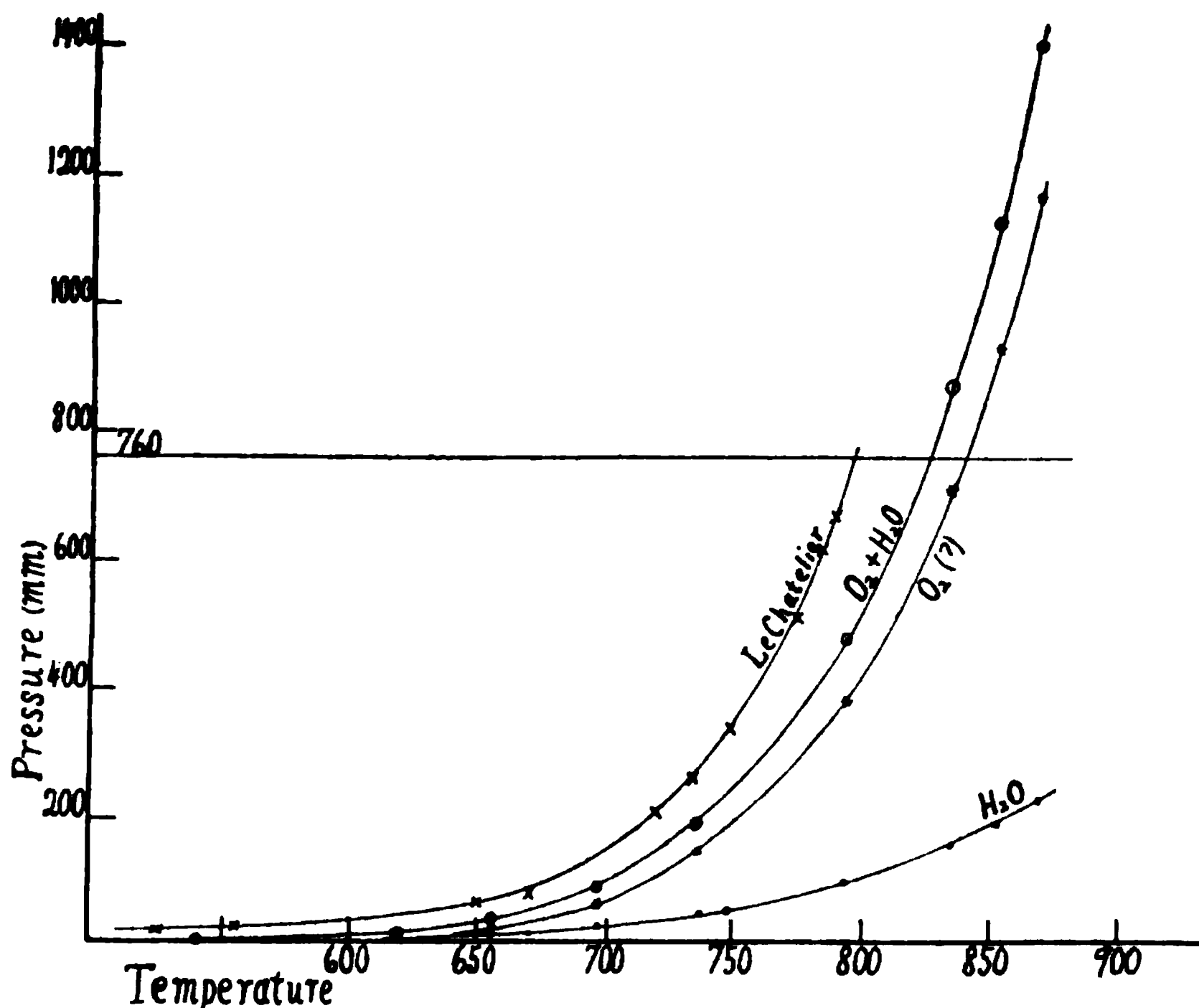


Fig. 3.

where C for oxygen is 2.8 when p is expressed in atmospheres. Q is the heat of reaction at constant pressure, and at temperatures not too far removed from absolute zero. Heats of reaction determined at ordinary temperatures will serve in approximate solutions, but the value calculated above, 37420 cals., will have to be recalculated to low temperatures before it can be substituted in the Nernst equation. This recalculation can be made by the relation involved in the Nernst equation, and which becomes apparent on comparing the value of $\frac{d \log p}{dT}$ obtained from that equation with the value obtained from the van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{Q_r}{RT^2},$$

the result giving the relation

$$Q_r = Q + 3.5T,$$

where Q_r is the heat of reaction at high temperatures, and Q that at low temperatures, or, more strictly, absolute zero. In the measurements from which Q_r has here been calculated, the mean temperature is about

1050 absolute, so that $Q = 33560$. The Nernst equation then becomes

$$\log p = \frac{-33560}{4.571 T} + 1.75 \log T + 2.8$$

which gives the observed pressures very closely if the constant is 1.278 instead of 2.8. In view of the possible variation in the composition of the solid phases, the agreement may be regarded as all that could be expected. If the above partial pressures of steam are too low, as is very probable, the constants would be still closer to 2.8.

This investigation serves to emphasize one point which has been neglected in most work upon heterogeneous equilibria, namely, that it is necessary to determine the nature of the phases involved in a heterogeneous equilibrium before measurements of dissociation pressures are of final value. Dissociation pressures of divariant systems are of little use.

Summary.

1. In the thermal dissociation of barium peroxide it has been shown that solid solutions of the oxide and peroxide in each other are formed. The effect of this upon the pressure as oxygen is removed is indicated, and the limits shown between which the system is univariant. The effect of the moisture necessarily present is also shown.

2. The conditions necessary to obtain a quantitative yield of barium peroxide from oxide are explained.

3. The conditions are indicated which would be necessary for the complete reversal of the equilibrium.

4. The dissociation pressures have been measured in the interval where the system is univariant, *i. e.*, where saturated solutions of the oxides are present, and are given closely by the equation

$$\log p = -6850/T + 1.75 \log T + 3.807,$$

where p is expressed in mm. and T is absolute temperature.

5. The heat of the reaction at constant pressure and an average temperature of 775° is calculated to be 35370 cal.

6. Assuming that the partial pressure of steam present is the same as that given by barium hydroxide alone, as given by the measurements of J. Johnston, the partial pressure of the oxygen is calculated. From these values the heat of dissociation of the solid solutions is calculated to be 37420 cal.

7. According to the formula of Nernst, this heat of reaction becomes 33560 cal. at absolute zero, which agrees with the Nernst approximation formula for calculating decomposition pressures in heterogeneous equilibria except that the constant must be 1.278 instead of 2.8, as given by Nernst. The agreement is all that might be expected, considering the possible variation in the composition of the solid phases.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

[SECOND PAPER.]

THE ANALYSIS OF PHOSPHORUS TRIBROMIDE.

BY GREGORY PAUL BAXTER, CHARLES JAMES MOORE AND ARTHUR CLARENCE BOYLETON.

Received January 12, 1912.

In a recent investigation by Baxter and Jones¹ upon the atomic weight of phosphorus by the analysis of trisilver phosphate, the constant in question was found to have the value 31.04 if silver has the atomic weight 107.88, or 31.03 if silver is given the value 107.87. While this result is in good accord with those of most earlier experimenters in the same field, Ter Gazarian,² on the other hand, from the density of phosphine, has recently obtained a considerably lower value, 30.91. So large a difference as this obviously needs explanation, and the most promising method of solving the problem seemed to be to analyze some other compound of phosphorus.

In the research upon silver phosphate some uncertainty was introduced by the fact that the salt contains only 7.7% of phosphorus, so that the percentage error in determining the molecular weight of silver phosphate is many times multiplied in the calculation of the atomic weight of phosphorus. In this respect phosphorus tribromide is somewhat better suited for the purpose, since it contains 11.5% of phosphorus. Hence, in spite of very considerable difficulties in the preparation of the tribromide in a pure state, and in its analysis, we were led to choose this substance for further investigation of the subject.

In outline the method followed was to synthesize phosphorus tribromide by the action of pure, dry bromine on pure, dry phosphorus in a vacuum. The product, which contained a slight excess of bromine, was fractionally distilled in a vacuum, and as soon as the excess of bromine had been eliminated various fractions were collected and analyzed for bromine in the usual way, after decomposition with water and oxidation of the phosphorous acid was produced.

Purification of Materials.

Water.—All the water used in this research was prepared from the laboratory supply of distilled water by further distillation, first from an alkaline permanganate solution, and then a second time, after the addition of a trace of sulfuric acid, through a block-tin condenser. No rubber or cork was used in the connection between the condenser tube and the Jena glass still.

Ammonia.—The best commercial ammonia was distilled into the purest water.

¹ *Proc. Am. Acad.*, 45, 137 (1910). *THIS JOURNAL*, 32, 298. *Z. anorg. Chem.*, 66, 97.

² *J. chim phys.*, 7, 337 (1909); 9, 101 (1911).

Nitric Acid.—C. P. concentrated acid was distilled through a platinum condenser, with rejection of the first two-thirds of the distillate. It was always carefully tested in a nephelometer for traces of halogens.

*Bromine.*¹—This substance was freed from all but a trace of chlorine by distillation from solution in a concentrated solution of potassium bromide. The product was next converted into potassium bromide by addition to a solution of recrystallized potassium oxalate. In order to remove iodine the solution of potassium bromide was boiled for some time, with the occasional addition of small amounts of the partially purified bromine which had been saved for this purpose. Toward the end of the boiling several small portions of potassium permanganate and sulfuric acid were added to remove last traces of iodine. Next the solution was evaporated to dryness and the dry salt was fused in a large platinum crucible to destroy organic matter. From the fused potassium bromide bromine was prepared as needed by solution in water and the addition of sufficient potassium permanganate and sulphuric acid to oxidize three-fourths of the bromide. In this process the bromine was distilled a second time from a bromide, and since this bromide was already nearly pure, last traces of chlorine must have been eliminated from the product. The bromine was separated as far as possible from water, and was dried by resublimed phosphorus pentoxide, from which it was distilled immediately before use. A quantity of bromine which had been thus treated was evaporated on a steam bath in a glass dish, which was then tested for residual phosphoric acid with negative results.

Phosphorus.—The method used for purifying the phosphorus was distillation with steam. In the case of the phosphorus from which the tribromide for the first series of analyses was prepared, the distillation was assisted by a current of carbon dioxide, and was not repeated. The phosphorus used for the second and third series of analyses was twice distilled with steam, the greater portion at atmospheric pressure, a small portion at reduced pressure, in an apparatus constructed wholly of glass. The purified material was preserved under water until used. Portions of these specimens were carefully tested for arsenic by the Berzelius-Marsh method and were found to contain less than one part in one million of the latter element. We are indebted to Mr. W. A. Boughton for carrying out these tests.

Silver.—Pure silver was prepared by methods which have already been found to be very effective. Since these methods have been described in detail several times in papers from this laboratory,² only a

¹ For a discussion of methods for purifying bromine see Richards and Wells, *Proc. Am. Acad.*, 41, 440 (1906). Baxter, *Ibid.*, 42, 204 (1906); *THIS JOURNAL*, 28, 1325; *Z. anorg. Chem.*, 50, 392.

² See especially Richards and Wells, *Pub. Car. Inst.*, No. 28, 16 (1905); *THIS JOURNAL*, 27, 472; *Z. anorg. Chem.*, 47, 70.

brief outline of the procedure is given here. Heterogeneous silver residues were reduced with zinc and sulfuric acid, and thoroughly washed with water. The metal was dissolved in nitric acid, and silver chloride was precipitated by a large excess of hydrochloric acid. After the precipitate had been washed it was dissolved in ammonia and reprecipitated with hydrochloric acid. The resulting chloride was reduced with an alkaline sugar solution and the metal was fused on charcoal. After cleansing with sand and etching with nitric acid, the buttons were dissolved in nitric acid, and the metal was precipitated with pure ammonium formate. The thoroughly washed product was fused with a blowpipe on a crucible of the purest lime. Electrolytic deposition with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons followed, and the electrolytic crystals were fused in a current of pure hydrogen on a boat of the purest lime provided with compartments so that the resulting buttons weighed from two to ten grams. After the buttons had been etched with nitric acid until their surfaces were uniformly crystalline, they were thoroughly washed with ammonia and pure water, and finally heated to 400° in a vacuum. The pure silver was preserved in a desiccator over fused potassium hydroxide.

Hydrogen Peroxide.—Merck's "Perhydrol," containing 30% hydrogen peroxide, was found to be free from sulfuric acid and halogens and to leave no residue upon evaporation. Hence it was employed without further treatment.

Nitrogen.—Atmospheric nitrogen free from oxygen was obtained by Wanklyn's well known method of passing air through very concentrated ammonia solution, and then over hot copper gauze in a hard glass tube. The excess of ammonia was removed by scrubbing with a dilute solution of sulfuric acid in three large gas-washing bottles. Since hydrogen is formed by the catalytic decomposition of a portion of the excess of ammonia, this impurity was oxidized in a hard glass tube filled with red hot copper oxide, and the gas was then dried in six towers filled with beads drenched with concentrated sulfuric acid and a long tube filled with resublimed phosphorus pentoxide. Finally the gas was passed through a third hard glass tube filled with hot copper to combine with any last trace of oxygen. The apparatus in which these operations were carried out was constructed entirely of glass with ground glass connections throughout.

Preparation of Phosphorus Tribromide.

Much time was consumed in finding a satisfactory method of preparing pure phosphorus tribromide. It was obvious at the outset that the substance must be rigorously protected from access of moisture, in order to avoid the formation of hydrobromic and phosphorous acids. This object was most simply gained by synthesizing the tribromide in a vacuum

from bromine and phosphorus which were initially dry. But since phosphorus dissolves in its tribromide, and can not be readily separated from the latter substance by distillation, an excess of bromine was added at the beginning. Fortunately it was necessary to add only a slight excess of bromine, since a surprisingly small amount of phosphorus pentabromide can be detected in the tribromide by its darker color, especially at high temperatures. This dark color is undoubtedly due in large part to dissociation of the pentabromide into tribromide and bromine. The comparatively easy elimination of the pentabromide from the tribromide also depends upon this dissociation, for the free bromine can be removed by distillation in the first fractions.

At first the attempt was made to remove the excess of bromine by distillation from red phosphorus. But either the red phosphorus still contained traces of the yellow modification, or else the red modification dissolved in the tribromide and vaporized with it when distilled (possibly as a lower bromide¹). At any rate the tribromide prepared in this way contained far too little bromine, as was shown by the results of its analysis.

Much better results were obtained by simple distillation in a vacuum. Although the boiling point of the tribromide is thus much lowered, the dissociation of the pentabromide is sufficiently complete to secure rapid elimination of the excess of bromine. As stated before, the disappearance of the bromine can be followed by the color of the distillate and residue. If material is collected for analysis as soon as the bromine has apparently been eliminated, it should yield at any rate a minimum value for the atomic weight of phosphorus, unless decomposition of the tribromide into a lower bromide occurs during the distillation. In the latter case, however, the composition of different fractions of the distillate would probably not be constant.

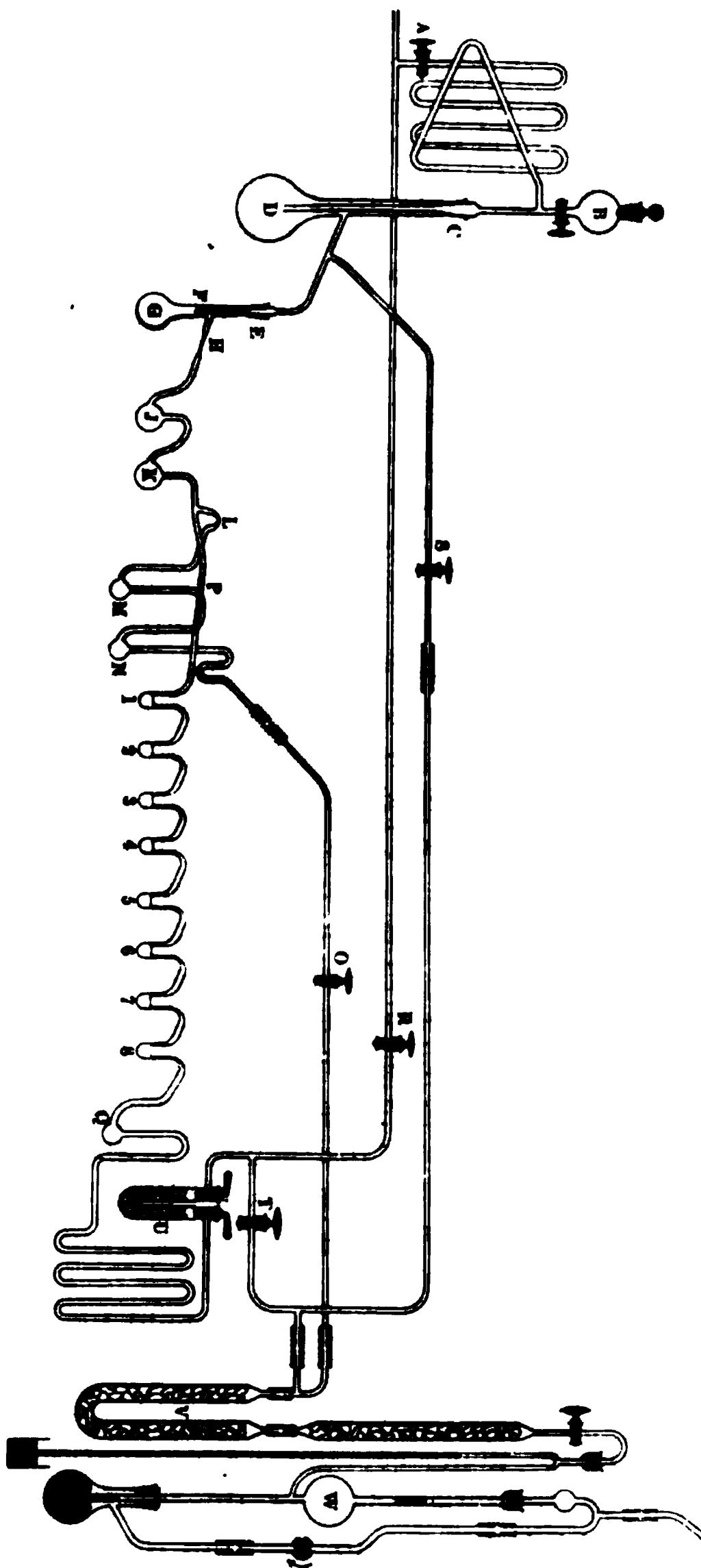
The synthesis of the tribromide was effected in an apparatus constructed entirely of glass shown in the figure on page 263. About 14 grams of pure phosphorus were freed as completely as possible from water by cooling and pressing between folds of hardened filter paper. The phosphorus was weighed to a centigram and placed in the distilling flask D, which had previously been filled with nitrogen through the stopcock A. The flask was then fitted to the separating funnel B by means of a well ground and polished joint, C, but it was not connected to the remainder of the apparatus at E, and the capillary tube F opened into the air.

In order to dry the phosphorus completely, the flask was surrounded with boiling water and for four hours a slow current of pure, dry nitrogen was forced in at A and flowed out at the end of the constricted tube F. The melted phosphorus was agitated from time to time by shaking the

¹ Besson and Fournier, *Compt. rend.*, 150, 120 (1910).

flask in order to liberate any steam which might have been entangled mechanically and to bring new material to the surface of the phosphorus. During this operation a portion of the phosphorus distilled into the cool tube F, and a small amount was vaporized into the air. Probably, too, a small amount of acids of phosphorus was produced since slight oxidation of the phosphorus necessarily took place while it was being introduced into the flask. As soon as the phosphorus had been dried in this way, the end of the constricted tube F was sealed, the stopcock A was closed, and the flask, after being cooled, was exhausted as completely as possible through the stopcock S by means of the Töpler pump W. All the ground glass joints were made gas-tight by means of a minimum quantity of syrupy phosphoric acid, and outside this, to prevent the absorption of moisture, soft paraffin was smeared.

Next the calculated amount of pure, dry bromine was measured from a buret into the separatory funnel B and the funnel was stoppered. After cooling the flask containing the phosphorus with ice water to reduce the violence of the reaction, bromine was slowly admitted. The rapid evaporation of a portion of the bromine produced the solidification of the remainder. This solid bromine, upon falling into the flask, reacted violently with the phosphorus until a considerable amount of tribromide had been formed. As



soon, however, as sufficient tribromide had been produced to dissolve the unchanged phosphorus the action became much less violent so that the bromine could be introduced more rapidly.

When nearly the theoretical amount of bromine had been used, the flask D was immersed in hot water in order to decompose a small amount of solid pentabromide which formed in the upper part of the flask. The bromine thus liberated diffused to the bottom of the flask, where it combined with the residual phosphorus dissolved in the tribromide. More bromine was then admitted in very small portions until the warm tribromide acquired the reddish color which indicated an excess of bromine. The end of the reaction can be determined so sharply by the color that the excess of the bromine probably never amounted to more than a few hundredths of a gram, whereas nearly one hundred and twenty-five grams of bromine in all were used in each preparation.

When it was certain that an excess of bromine had been added, the flask D with the tribromide was surrounded with ice water and nitrogen was allowed to enter through A, until the pressure inside the flask was greater than atmospheric. The end of the tube F was then broken off, and the remainder of the apparatus, which had previously been filled with dry nitrogen, was attached by the ground joint E. The flasks D, G, J, K, M and N were next exhausted through O, while the stopcocks A, R, S and T were closed. In order to prevent access of bromine to the mercury of the Töpler pump, a U-tube, V, filled with fused potassium hydroxide was located between the pump and the remainder of the apparatus, and this U-tube was cooled with concentrated calcium chloride solution and ice.

During the fractional distillation of the tribromide to remove the excess of bromine it was highly desirable to protect the bulbs 1 to 8, in which the tribromide was eventually to be collected, from contact with the first fractions. This was effected by passing the first fractions through the side tube L into the bulbs M and N, while the bulbs 1 to 8 were cut off from the rest of the apparatus by the valve P. This valve was so perfectly made that it was nearly gas-tight with no lubricant. Nevertheless, in addition, nitrogen was maintained at atmospheric pressure on the far side of the valve, so that the slight leakage produced a slow reverse current of nitrogen through the valve into the pump by way of the bulbs M and N.

Under as low a vacuum as could be obtained with the pump the tribromide was first distilled from D to G by surrounding D with boiling water and G with ice water. A small residual fraction was left in D, in order to make certain the elimination of phosphorous acid and possible oxybromide. During this distillation any phosphorus which had originally distilled into the tube F and still remained uncombined was

converted into tribromide by the excess of bromine. A second similar distillation from G to J and K followed, with rejection of the last few grams in G. The material invariably contained an excess of bromine at this point. The capillary tube H was now sealed with a blowpipe and the flasks D and G were thus disconnected from the apparatus. Next the bulbs M and N were cooled with ice and the tribromide in J was boiled while the bulb K was gently warmed. The vapor from J in bubbling through the warm liquid in K carried with it all the excess of bromine in both bulbs. Furthermore, it is probable that if the tribromide contained a trace of hydrobromic acid, the latter substance was eliminated at the same time as the bromine. The distillate collected in M and N as tri- and pentabromide. As soon as ten grams of material had been distilled from J and K the residue, amounting to considerably more than one hundred grams, was nearly colorless; nevertheless five times as much more was distilled into M and N before this part of the apparatus was sealed off at the capillary L. Thus when the stopcock O was closed, the impure distillate was entirely cut off from the remainder of the apparatus.

The bulbs 1 to 8 were then exhausted by opening the stopcocks of the U-tube U and at the point T, while R was closed. The U-tube contained resublimed phosphorus pentoxide to prevent the possibility of back diffusion of moisture into the bulbs. The valve P, into which a piece of soft iron had originally been sealed, could now be pulled from its seat by means of a magnet so that the bulbs J and K were connected with the pump through the bulbs 1 to 8.

In distilling the remainder of the tribromide into the small bulbs the one nearest the pump was filled first by surrounding it with ice water, while the other seven were immersed in beakers filled with boiling water. As soon as bulb 8 was three-fourths filled with material, bulb 7 was cooled with ice water, and so on until all were filled. All the residual material in J and K was distilled into bulb 1.

The train of bulbs 1 to 8 was next sealed off with a blowpipe at the capillaries, and the individual bulbs were separated from the connecting tubes by sealing the capillary tubes. Great care was taken in sealing the capillaries to avoid decomposing the tribromide, by first heating them gently to evaporate any tribromide with which they might be wet. There never was any sign of decomposition of the tribromide during this process.

The final samples of the tribromide were almost colorless when cold, but the very slight yellowish tint of the cold substance was materially increased by a rise in temperature. Since no difference in color could be detected between the first and last samples collected, it seems probable that phosphorus tribromide really possesses a slight yellowish tint.

Two series of samples of tribromide were distilled and sealed in bulbs from two different preparations of material. Ten fractions were collected in the first series and eight in the second.

In a third preparation the removal of the bromine was accelerated by distillation from metallic silver. The bulbs J and K were partly filled with fine electrolytic crystals of the purest silver which had been freed from moisture by ignition in a vacuum. After the tribromide had been distilled into J and K, and the excess of bromine had been distilled into M and N, the capillary tube L was sealed as described before. Then the bulbs J and K with the residual tribromide were warmed for some time with constant shaking before the tribromide was finally distilled into the collecting bulbs.

The Determination of the Weight of the Tribromide and its Analysis.

In the analysis of the tribromide it was first decomposed with water, and then the bromine was precipitated as silver bromide. The reducing effect of phosphorous acid upon silver salts is well known, so that the necessity was obvious of oxidizing the phosphorous acid. This operation was a somewhat delicate one, however, since the hydrobromic acid also is easily oxidized, with consequent loss of bromine. Hydrogen dioxide was eventually found to be the safest oxidizing agent, although its action on the phosphorous acid is not particularly rapid. In preliminary experiments the bulb of tribromide was broken under water and the oxidation was then effected by hydrogen peroxide in dilute nitric acid solution. In the final experiments the method of breaking the bulb under an ammoniacal solution of hydrogen dioxide was employed, since in this way the greater part of the oxidation was almost instantaneously effected. Then after time the solution was acidified with nitric acid and allowed to stand for a further period. Even then it is probable that oxidation is not quite complete, for if the bromine is precipitated with any considerable excess of silver nitrate, even in the presence of much nitric acid, the silver bromide is perceptibly discolored. On the other hand, if the amount of silver salt used is very nearly equivalent to the bromide present, the precipitate retains its lemon-yellow color even when left for days under the solution.

Since the determination of the weight of the tribromide and its analysis are so intimately connected, they are described together.

The weight of the tribromide was found in each analysis by weighing the bulb with its contents, and then, after breaking the bulb, collecting and weighing the glass. The bulb was first carefully cleaned on the outside and dried, and left in a desiccator over sulphuric acid for at least twenty-four hours. Its weight in air was then found by substituting standardized weights for the bulb on the balance. The buoyant effect of the air was estimated by finding the volume of the bulb

in the usual way from the loss in weight under water of known temperature. The conditions of the atmosphere were taken into account in calculating the buoyant effect of the air on the bulb and weights. Since the bulb was exhausted when sealed no correction is necessary for the space in the bulb not filled with liquid.

After the bulb had been weighed and its volume determined, it was placed in a 300 cc. thick-walled Erlenmeyer flask together with somewhat over 100 cc. of redistilled ammonia and 10 cc. of pure 30% hydrogen dioxide. A glass stopper, which had been carefully ground into the neck of the flask, was inserted, and the flask was shaken violently enough to break the bulb. The heavy tribromide reacted quietly at the bottom of the aqueous solution, until at the end of about five minutes decomposition was complete. The flask was then allowed to stand twenty-four hours, with occasional shaking. This long standing was necessary to allow a small quantity of ammonium bromide fumes to be collected in the aqueous solution.

The flask, cooled to produce inward pressure, was next carefully opened and the solution was filtered into a three-liter ground-stoppered precipitating flask, while the particles of glass were collected upon a small filter paper. This filter was very thoroughly rinsed with pure water until the filtrate and washings amounted to about 1200 cc.

In order to find the weight of the glass the filter was burned at as low a temperature as possible in a weighed platinum crucible. When the weight of the glass, corrected to vacuum, was subtracted from the corrected weight of the bulb and the tribromide, the weight of the tribromide in vacuum was obtained.

In order to make sure that this method of finding the weight of the glass was a satisfactory one, it was tested by several blank experiments with bulbs containing no tribromide. These bulbs were first weighed in the air unsealed, and then were treated in exactly the same way as bulbs containing tribromide. In two cases the fragments of the bulbs were collected upon a weighed Gooch-Munroe-Neubauer crucible. In the first three, however, the glass was collected upon a small filter paper as in the analyses:

Weight of bulb. Grams.	Weight of glass recovered. Grams.	Difference. Gram.
1.20098	1.20097	—0.00001
0.99814	0.99813	—0.00001
1.01851	1.01846	—0.00005
1.12986	1.12994	+0.00008
1.08438	1.08441	+0.00003

Since in every experiment the weight of the glass collected agrees with that of the bulb within 0.00008 gram and is never more than 0.00005 gram less than that of the bulb, it is evident that no important amount

of glass is lost either by passing through the filter paper or by solution in the ammoniacal liquid.

The filtrate containing ammonium bromide was next acidified by the addition of about 40 cc. of concentrated nitric acid diluted to about 300 cc. Since bromine was sometimes locally set free during the addition of the acid, the acid solution was poured into the bromide through a thistle tube, the stem of which extended to the bottom of the flask. Thus, although bromine might be set free at the dividing surface between the bromide and the nitric acid, no bromine ever reached the upper surface of the liquid, owing to the unoxidized phosphorous compounds in the bromide solution. The thistle tube was thoroughly rinsed into the flask, the stopper of the flask moistened and put in place, and the flask gently agitated to mix the solutions. It was then allowed to stand for forty-eight hours. In no case was there any evidence that bromine was permanently set free by the nitric acid, for after the mixing of the solutions they were always colorless, and when the flasks were opened after two days' standing no odor of bromine could be detected, although 0.00001 g. is readily perceptible in 3 liters of air.¹

During the standing in acid solution the oxidation of the residual phosphorous acid progressed, but even at the end of the period it was not quite complete. Precipitation of the silver bromide immediately after acidification invariably resulted in darkened salt, but after forty-eight hours an apparently pure product was obtained, if no appreciable excess of silver was used.

The bromine in each sample was determined in two ways: first, by finding the amount of silver necessary to combine with it; second, by weighing the silver bromide formed. Both determinations could be carried out with the same sample of tribromide.

A quantity of silver equivalent to the tribromide within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. After the silver solution had been freed from oxides of nitrogen by dilution and heating, about 40 cc. of concentrated nitric acid were added and the whole was diluted to a volume of about one liter. The silver solution was then quantitatively added to the bromide solution, with constant agitation, and the stoppered precipitating flask was allowed to stand for several days with occasional shaking. When the precipitate had coagulated and settled so completely that the supernatant liquid was apparently clear, portions of the solution were tested in a nephelometer² for excess of bromide or silver. As a matter of fact, bromide was always found in slight excess. The deficiency of silver,

¹ Baxter, Thorvaldson and Cobb, *THIS JOURNAL*, 33, 329 (1911).

² Richards and Wells, *Am. Chem. J.*, 31, 235 (1904); 35, 510 (1906).

which was never more than a very few tenths of a milligram, was made up as nearly as could be estimated by means of a hundredth-normal solution of silver nitrate. After thorough shaking and standing until the solution was perfectly clear, tests for excess of bromide or silver were again made. If necessary, this process was repeated, until eventually the amounts of bromide and silver were equivalent. Owing to the slight solubility of silver bromide at this point, the solution remained essentially clear, even in the nephelometer, when either bromide or silver solution was added.

The solution was now allowed to stand for a week with occasional shaking and then was tested again in the nephelometer. Usually a deficiency of one- or two-tenths of a milligram of silver was found, owing apparently to extraction of occluded soluble bromide from the silver bromide. This deficiency of silver was supplied and the solution was left for another week before being tested again, and this process was repeated until in the course of a week no further change in the solution took place. In a few analyses the solutions were tested over a period of four months, but in no case was any appreciable change in the end point found after it had remained constant for a week. In most cases the final end point was reached within two weeks.

The difficulty from occlusion of the silver bromide was unexpected since it has not been met to the same extent in other similar cases in this laboratory.¹ In fact, it was not discovered in this research until Analyses 1, 2, 5, 9, and 10 of Series I had been completed. After its discovery several unsuccessful attempts were made to eliminate the occlusion. In Analyses 6 and 19 the solutions of ammonium bromide and silver nitrate were each diluted to nearly four liters before precipitation. In these two analyses, on account of the large size of the precipitating vessel, no attempt was made to collect the silver bromide, since the results of the comparison with silver were no different from those obtained in more dilute solution. Although occlusion of bromide seemed to be diminished in extent by this modification, the time necessary for the establishment of equilibrium was not materially lessened. Even in Analysis 6, where the bromide solution was added to the silver solution, the occluded substance seemed still to be a soluble bromide. Cooling the solutions to the temperature of ice-water before precipitation seemed to accentuate the occlusion.

As soon as a permanent end point had been reached, the precipitate was thoroughly washed by decantation with pure water and collected upon a weighed Gooch-Munroe-Neubauer crucible. The crucible and contents were heated gradually to nearly 200° and were kept at that

¹ See, however, Richards and Staehler, *THIS JOURNAL*, 29, 632 (1907); *Ber.*, 39, 3618.

temperature for eighteen hours or more. Then they were cooled and weighed by substitution for a similar counterpoise. In order to find the moisture retained by the dried precipitate it was transferred as rapidly and completely as possible to a small porcelain crucible which was immediately weighed with its cover. Then the silver bromide was fused by heating the small crucible contained inside a much larger one. During the solidification of the bromide the system was carefully rotated so that the fused bromide was stirred and caused to solidify in a thin layer. The loss in weight on fusion was then determined. This loss seldom amounted to more than 0.001% of the weight of the salt. The fused bromide was always clear and light yellow, whereas an astonishingly small percentage of impurity is capable of producing perceptible darkening of the salt.

Since silver bromide possesses an appreciable solubility in water,¹ the

SERIES I.							
Ag = 107.880.			PBr ₃ : 3Ag.			Br = 79.916.	
No. of analysis.	Fraction of PBr ₃ .	Weight of PBr ₃ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Deficiency of Ag. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio PBr ₃ :3Ag.	Atomic weight of phosphorus.
1	1	5.95293	7.11494	0.00010	7.11504	0.836668	31.031
2	2	4.71056 ^a	5.63017	0.00005	5.63022	0.836657	31.028
3	3	4.72373	5.64553	0.00030	5.64583	0.836676	31.034
4	4	6.47622	7.74048	0.00000	7.74048	0.836669	31.031
5	5	4.61956	5.52120	0.00020	5.52140	0.836665	31.030
6	8	7.62060	9.10809	0.00040	9.10849	0.836648	31.025
7	9	3.83321	4.58153	0.00010	4.58163	0.836648	31.025
8	10	4.72578	5.64800	0.00035	5.64835	0.836666	31.030
Average.....						0.836660	31.031

SERIES I.							
PBr ₃ : 3AgBr.							
No. of analysis.	Fraction of PBr ₃ .	Weight of PBr ₃ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	AgBr from filtrate and washings. Gram.	Corrected wt. of AgBr in vacuum. Grams.	Atomic weight of phosphorus.
9	1	5.95293	12.38515	0.00015	0.00060	12.38560	31.035
10	2	4.71056	9.79992	0.00011	0.00077	9.80058	31.039
11	3	4.72373	9.82782	0.00018	0.00066	9.82830	31.031
12	4	6.47622	13.47392	0.00015	0.00051	13.47428	31.036
13	5	4.61956	9.61089	0.00005	0.00059	9.61143	31.034
14	9	3.83321	7.97524	0.00006	0.00045	7.97563	31.025
15	10	4.72578	9.83205	0.00004	0.00060	9.83261	31.029
Average.....						0.480629	31.033

¹ Böttger, *Z. physik. Chem.*, 46, 602 (1903), 0.00008 g. per liter at 20°. Kohlrausch, *Ibid.*, 50, 536 (1905), 0.00011 g. per liter at 21°.

SERIES III.								
Ag = 107.880.			PBr ₃ : 3AgBr.			Br = 79.916.		
No. of analysis.	Fraction of PBr ₃ .	Weight of PBr ₃ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	AgBr from filtrate and wash waters. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio PBr ₃ :3AgBr.	Atomic weight of phosphorus.
32	1	4.39626	9.14614	0.00018	0.00067	9.14663	0.480643	31.040
33	3	7.07758	14.72594	0.00017	0.00055	14.72642	0.480604	31.019
34	4	4.19854	8.73548	0.00020	0.00058	8.73586	0.480610	31.022
35	6	7.26540	15.11696	0.00020	0.00049	15.11725	0.480603	31.018
36	8	7.75072	16.12689	0.00032	0.00080	16.12737	0.480594	31.013
Average.....							0.480611	31.022
Average of Series I, II and III.							0.480623	31.029

filtrate and wash waters were evaporated to small bulk, and after a slight precipitate of silicic acid had been removed by filtration, were diluted to 100 cc. Portions of the solution were then analyzed for silver by comparison in the nephelometer with standard silver nitrate solutions, after the addition of an excess of bromide. In each analysis the amount obtained in this way exceeds slightly the amount to be expected from the solubility of silver bromide, owing doubtless to colloidal silver bromide which escaped the crucibles. A correction for the silver found in this way, estimated as bromide, was added to the weight of the main mass of silver bromide.

The precipitating flask was rinsed with ammonia, and, if the solution was found to contain silver, the quantity was determined in a similar fashion in the nephelometer and a correction applied.

The preceding tables contain the results of all the analyses which met with no accidents. A considerable portion of the preliminary work on the methods of preparation and analysis was done by A. C. Boylston. The perfection of the apparatus and methods and all the final preparations and analyses were made by C. J. Moore.

Weighings were made on a No. 10 Troemner balance sensitive to a very few hundredths of a milligram, while the gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.¹

Vacuum corrections were applied as follows:

	Specific gravity.	Vacuum correction.
Weights.....	8.3	+0.000145
AgBr.....	6.47	+0.000041
Ag.....	10.49	—0.000030
Glass.....	2.5	+0.000335

The following table, which gives the ratio of silver used to silver bro-

¹ THIS JOURNAL, 22, 144 (1900).

mide obtained in the same analysis, strengthens the view that the precautions taken to prevent reduction of the silver salts by the phosphorous compounds and occlusion by the silver bromide were effective:

Analyses.	Ag : AgBr.
1 and 9	0.574461
2 and 10	0.574478
3 and 11	0.574446
4 and 12	0.574463
5 and 13	0.574462
7 and 14	0.574454
8 and 15	0.574451
16 and 22	0.574486
17 and 23	0.574473
18 and 24	0.574466
20 and 25	0.574473
21 and 26	0.574478
27 and 32	0.574470
28 and 33	0.574448
29 and 34	0.574472
30 and 35	0.574446
31 and 36	0.574431
<hr/>	
Average.....	0.574462

Although the average result is very slightly higher than the value which has already been shown by Baxter¹ to be the most probable one, 0.574453, the difference, which is less than 0.002%, is too small to be significant.

In examining critically the results recorded in the foregoing tables it should first of all be noted that a given percentage error in the experimental work is multiplied nine times in the calculation of the atomic weight of phosphorus; that is, an experimental error of one one-hundredth of a per cent. affects the atomic weight of phosphorus by 0.027 unit. The highest value for the atomic weight of phosphorus in these tables is 31.040, the lowest 31.013, a difference corresponding exactly to one one-hundredth of a per cent. in the experimental work. On the whole, however, the agreement of the results is better than this, since, of the thirty-six results, twenty-seven fall between the limits 31.035 and 31.021, a difference only half as large. In other words, the different specimens of material seem to be identical as far as the method is capable of testing this point.

In each series, if the first fraction, that of the highest number, 8 or 10, contained an excess of bromine, it would have yielded too low a result, while if decomposition occurred during the distillation, with the possible production of lower bromides of phosphorus, the residual fraction, 1, would have yielded too high a result. The only differences in each series,

¹ *Proc. Am. Acad.*, 42 (1906). *THIS JOURNAL*, 28, 1322. *Z. anorg. Chem.*, 50, 389.

however, seem to be purely accidental. Furthermore, the three series yield average results in practical unanimity.

In the following table the final average of this research is compared with that of Baxter and Jones with silver phosphate:

	Ag = 107.88.	Ag = 107.87.	Ag = 107.86.
PBr ₃	31.027	31.024	31.021
Ag ₃ PO ₄	31.04	31.03	31.02

Summary of Results.

1. A method is described for the preparation of pure phosphorus tribromide.

2. It is shown that the precipitation of the halogen of phosphorus halides after decomposition with water, can safely be done only after the oxidation of the greater portion of the phosphorous acid produced.

3. A method is described for the determination of the bromine in phosphorus tribromide by comparison with silver and as silver bromide.

4. The molecular weight of phosphorus tribromide referred to silver 107.88 is found to be 270.775, whence phosphorus has the atomic weight 31.027. If silver is taken at 107.87, the atomic weight of phosphorus becomes 31.024. These values agree very closely with those found by the analysis of silver phosphate by Baxter and Jones.

An attempt to prepare and analyze phosphorus trichloride in a similar manner is now under way in this laboratory.

We are particularly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS.

THE REDUCTION OF VANADIC ACID IN CONCENTRATED SULFURIC ACID SOLUTION BY HYDROGEN PEROXIDE AND BY PERSULFATES.

By J. R. CAIN AND J. C. HOSTETTER.

Received January 4, 1912.

Gregory¹ recently described a colorimetric method for vanadium depending on the colors developed when concentrated sulfuric acid solutions of vanadium and strychnine are mixed. It seemed likely from his statements and from others in the literature that the strychnine colors develop only with pentavalent vanadium. We satisfied ourselves that quadrivalent vanadium compounds, at least, give no colors. However, concentrated sulfuric acid solutions of vanadium containing small amounts of the latter are very apt, from various causes, to become reduced to quadrivalent vanadium when carrying out Gregory's method, and as we desired to avoid the use of potassium chlorate, as recommended by him, we tested various oxidizing agents. Among others, hydrogen peroxide

¹ *Chem. News*, 100, 221 (1909).

was used. But, judging from the colors developed by treating with hydrogen peroxide and adding strychnine, the peroxide treatment was unsuccessful. This seemed so surprising that stronger solutions of vanadium peroxide in concentrated sulfuric acid were tested as to their behavior with hydrogen peroxide. To our surprise we found that vanadium pentoxide in such solutions was immediately and quantitatively reduced to the quadrivalent condition by the peroxide. This was shown on the one hand by the sudden color change from the orange or straw-color of sulfuric acid solutions of the pentoxide to the deep blue of the quadrivalent vanadium compounds, and on the other hand by titration against permanganate. Indeed, this affords a very convenient method for standardizing pure vanadium solutions. All that is necessary is to evaporate the solution with concentrated sulfuric acid until fumes are given off freely, cool, add a slight excess of 3% hydrogen peroxide, cover the flask and fume strongly for a few minutes more to destroy the excess of peroxide, after which the solution may be titrated against permanganate. We made some tests showing that molybdenum and titanium are not similarly reduced by hydrogen peroxide; also iron is not reduced.

Peroxides of zinc, barium, magnesium and sodium behaved in the same manner as hydrogen peroxide; however, the reduction succeeds best with the latter. Barium peroxide, particularly, should not be used where one is standardizing vanadium solutions, inasmuch as the resulting precipitate carries vanadium which would escape titration.

It was also found that concentrated sulfuric acid solutions of vanadium pentoxide could be reduced with persulfates. Our experiments were carried out with potassium and ammonium persulfates. Inasmuch as it is known that persulfates in concentrated sulfuric acid change more or less rapidly to Caro's acid, and since Caro's acid is sometimes made by adding hydrogen peroxide to concentrated sulfuric acid, it seemed quite likely that Caro's acid caused, or took part in, the reaction. Accordingly, a quantity of this reagent was prepared¹ by slowly dropping perhydrol into sulfuric acid (50% by volume) cooled by a freezing mixture. After allowing ten minutes for the system to reach a condition of equilibrium, the excess of peroxide was destroyed by permanganate. Now, on adding the reagent thus prepared to a concentrated sulfuric acid solution of vanadium pentoxide, the reduction took place, as expected, so there seems but little doubt that the reaction is really between Caro's acid and vanadium pentoxide. We have not investigated the mechanism of the reaction, but it seems quite possible that such an investigation would throw some light on the still rather obscure question as to the constitution of Caro's acid.

We have found no references in the literature, in hand-books nor in

¹ Baeyer and Villiger, *Ber.*, 34, 853 (1901).

text-books on quantitative analysis, to this reaction, and believe the observation to be new. It is of interest, perhaps, to note certain observations which show that some investigators have probably had this phenomenon accompanying others, without, however, fully recognizing or explaining it. Thus, Scheuer¹ analyzed barium and other pervanadates by treating them in a flask with dilute sulfuric acid, boiling until no more oxygen was given off, and measuring the amount of oxygen evolved. Hydrogen peroxide is liberated under these conditions and if the concentration of sulfuric acid is right, some or all of the vanadium may be reduced to the quadrivalent condition. Speaking of the analysis of barium pervanadate, Scheuer says, concerning the operation of boiling the solution to expel oxygen: "Dies ist beendet wenn die anfangs rote Lösung (primary action of peroxide on vanadium, giving pervanadic acid) eine hellgrüne Färbung angenommen hat." The "hellgrüne" color must have been that of a mixture of V_2O_4 and of V_2O_5 , due to a partial reduction of the V_2O_5 by hydrogen peroxide. However, Scheuer says "In die Filtrate fand sich noch die freie Vanadinsäure.," and then gives instructions for determining it by reducing with sulfur dioxide and titrating against permanganate. Also, Cammerer,² in preparing pervanadic acid by causing hydrogen peroxide to react with solid vanadium pentoxide, found that the aqueous solution of the reaction product, when evaporated on the steam-bath, deposited a greenish colored substance giving, in dilute sulfuric acid, a green solution which reduced permanganate. More recently, Trautmann,³ in analyzing ferrovanadium, fuses it with sodium peroxide, extracts the fusion with water and filters. The solution, which contains the vanadium and an excess of hydrogen peroxide, is acidified with sulfuric acid, and Trautmann states that at this stage he often observed a reduction, after boiling off the hydrogen peroxide. It seems very likely that here, also, conditions are sometimes right for reduction of vanadic acid by hydrogen peroxide.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

NEW COMPOUNDS OF SAMARIUM AND NEODYMIUM.

BY C. JAMES, F. M. HOBEN AND C. H. ROBINSON.

Received January 8, 1912.

The following compounds were prepared during a search for salts of the rare earths that might be useful for fractionating:

Samarium Ethylsulfonate $(C_2H_5SO_3)_6Sm_2 \cdot 6H_2O$.—Ethylsulfonic acid was heated nearly to boiling and small quantities of samarium oxide added

¹ *Z. anorg. Chem.*, 16, 289 (1898).

² *Chem. Ztg.*, 15, 958 (1891).

³ *Z. anal. Chem.*, 50, 371 (1911).

until no more oxide would dissolve. Finally a little more acid was added, the whole boiled for a short time, filtered and evaporated down on the water bath. The compound gradually crystallized out upon standing. The crystals were freed from the mother liquor by suction and washed with acetone.

This salt formed pale yellow crystals, very soluble in water and alcohol, but insoluble in acetone and ether. Upon heating, this substance charred and gave off a strong garlic odor.

Samarium ethylsulfonate lost all its water of crystallization when heated to 100° for four hours.

Calculated: Sm_2O_3 , 32.78; S, 18.09; H_2O , 10.16. Found: Sm_2O_3 , 32.70; S, 18.17; H_2O , 10.14.

Samarium Methylsulfonate $(\text{CH}_3\text{SO}_3)_6\text{Sm}_2 \cdot 7\text{H}_2\text{O}$.—This substance was prepared in a similar manner to the former sulfonate. The solution, after filtering and evaporating was allowed to stand for a day and a half. The crystals were dried as much as possible by suction and washed with acetone.

This sulfonate formed pale yellow crystals, very soluble in water and alcohol, only slightly soluble in acetone, and insoluble in ether.

Samarium methylsulfonate lost six molecules of water of crystallization after heating to 100° for some time.

Calculated: Sm_2O_3 , 34.97. Found: Sm_2O_3 , 35.15.

Samarium Propylsulfonate $(\text{C}_3\text{H}_7\text{SO}_3)_6\text{Sm}_2 \cdot 9\text{H}_2\text{O}$.—Obtained like the ethylsulfonate.

This compound did not crystallize well. It was filtered from the mother liquor by suction and well washed with ether. The result of this treatment was a powder, of small crystals, possessing a yellowish tint, soluble in water, alcohol and acetone but insoluble in ether.

The propylsulfonate, when heated for a long time at 100° , lost eight molecules of water of crystallization.

Calculated: Sm_2O_3 , 29.04. Found: Sm_2O_3 , 29.12.

Samarium Isobutylsulfonate, $(\text{C}_4\text{H}_9\text{SO}_3)_6\text{Sm}_2 \cdot 7\text{H}_2\text{O}$, was prepared by saturating isobutylsulfonic acid with samarium oxide, care being taken to have the solution acid before filtering and evaporating. The concentrated solution was allowed to stand over sulfuric acid for a few days. The crystals were separated and washed with ether.

Samarium isobutylsulfonate lost five molecules of water, when kept at 100° for two days.

Calculated: Sm_2O_3 , 27.90. Found: Sm_2O_3 , 27.97.

Samarium Camphorsulfonate, $(\text{C}_{10}\text{H}_{15}\text{OSO}_3)_6\text{Sm}_2 \cdot 10\text{H}_2\text{O}$.—This sulfonate was obtained as above. When sufficient of the salt had separated, the dish was removed from the desiccator, the crystals separated upon a small

Buchner funnel and washed with ether. The crystals were dissolved in alcohol and the solution allowed to crystallize, after which it was again well washed with ether.

Samarium camphorsulfonate formed a mass of very small crystals, white with only a faint yellow tint. It was very soluble in water, alcohol and acetone, but insoluble in ether.

This compound after heating for some time at 100° became nearly anhydrous.

Calculated: Sm_2O_3 , 18.67. Found: Sm_2O_3 , 18.61.

Samarium Methane-trisulfonate, $(\text{CH}(\text{SO}_3)_3)_2\text{Sm}_2 \cdot 16\text{H}_2\text{O}$.—A slightly acid solution of samarium oxide in methane-trisulfonic acid was evaporated and set aside to crystallize. The samarium compound separated very well after standing for a day. The crystals were drained and well washed with alcohol. They were yellowish, transparent, soluble in water but insoluble in alcohol, acetone and ether. This salt is very stable since it can be heated to high temperatures, with fuming nitric acid in sealed tubes, without decomposition taking place.

Samarium methane-trisulfonate lost two molecules of water after prolonged heating to 100° .

Calculated: Sm_2O_3 , 31.84. Found: Sm_2O_3 , 31.88.

Samarium 1,3,4-Meta-xylenesulfonate, $(\text{C}_6\text{H}_3(\text{CH}_3)_2\text{SO}_3)_2\text{Sm}_2 \cdot 7\text{H}_2\text{O}$.—A concentrated solution of samarium oxide in the xylenesulfonic acid crystallized after standing some time. The solid was drained and washed with acetone. It formed small, very pale yellow crystals, soluble in water and alcohol, insoluble in acetone and ether.

Calculated: Sm_2O_3 , 22.69. Found: Sm_2O_3 , 22.65.

Samarium Glycollate, $(\text{CH}_2\text{OH.COO})_6\text{Sm}_2$.—Samarium hydroxide was gradually added to cold glycollic acid. Upon heating the filtered solution the salt separated as a very dense precipitate which was almost insoluble in water.

Samarium glycollate differs from yttrium glycollate, inasmuch as the former is anhydrous while the latter contains two molecules of water of crystallization.¹

Calculated: Sm_2O_3 , 46.44. Found: Sm_2O_3 , 46.54.

Samarium Cacodylate, $((\text{CH}_3)_2\text{AsO}_2)_6\text{Sm}_2 \cdot 16\text{H}_2\text{O}$.—This substance was obtained by boiling a solution of cacodylic acid with samarium hydroxide. The last portions of samarium hydroxide were dissolved by the careful addition of more acid. Upon cooling, the solution crystallized. The whole was poured upon a Buchner funnel and the crystals washed with alcohol and dried.

The cacodylate forms white crystals which are soluble in hot water, insoluble in alcohol and acetone.

¹ Pratt and James, *THIS JOURNAL*, 33, 1330.

When kept at 100° for three hours all water of crystallization was lost.

Calculated: Sm_2O_3 , 24.73; H_2O , 20.43. Found: Sm_2O_3 , 24.81; H_2O , 20.43.

Samarium Ethylene-disulfonate, $(\text{C}_2\text{H}_4(\text{SO}_3)_2)_2\text{Sm}_2 \cdot 4\text{H}_2\text{O}$, was prepared by saturating ethylene disulfonic acid with samarium hydroxide. The solution was made slightly acid, filtered and evaporated. The salt separated well. It formed yellow transparent crystals, soluble in water, slightly soluble in alcohol and insoluble in acetone.

Calculated: Sm_2O_3 , 37.22. Found: Sm_2O_3 , 37.04.

Samarium Ethylglycollate, $(\text{C}_2\text{H}_5\text{O} \cdot \text{CH}_2\text{COO})_2\text{Sm}_2 \cdot 18\text{H}_2\text{O}$. — Separated from concentrated solution in large yellow transparent crystals which contained included mother liquor. An analysis showed the presence of eighteen molecules of water of crystallization. However, since there was doubt about mother liquor, the study of the rare earth ethylglycollates will be continued at an early opportunity, with larger amounts of material.

Samarium Citraconate, $\left[\begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{COO} \\ \parallel \\ \text{CHCOO} \end{array} \right]_2\text{Sm}_2 \cdot 12\text{H}_2\text{O}$. — Citraconic acid was saturated with samarium hydroxide, filtered and concentrated. The compound which separated out upon standing, was removed by suction and the mass of citraconate washed with alcohol and acetone.

Calculated: Sm_2O_3 , 38.72. Found: Sm_2O_3 , 38.88.

Samarium Sulfoacetate, $\left[\begin{array}{c} \text{CH}_2\text{SO}_3 \\ | \\ \text{COO} \end{array} \right]_2\text{Sm}_2$. — Samarium hydroxide rapidly dissolved in sulfoacetic acid. No crystals were obtained by evaporation and leaving over sulfuric acid. The solution merely formed a thick sticky mass.

Samarium Hydroxyethanesulfonate. — A concentrated solution of this compound would not crystallize when allowed to remain in a desiccator over sulfuric acid.

Neodymium Methylsulfonate, $(\text{CH}_3\text{SO}_3)_2\text{Nd}_2 \cdot 7\text{H}_2\text{O}$. — Methylsulfonic acid was saturated with neodymium oxide and filtered. The concentrated solution solidified to a crystalline mass, when left in a desiccator, over sulfuric acid. The crystals were broken up and well washed with ether. They were very soluble in water, soluble in alcohol and slightly so in acetone, but insoluble in ether. It lost six molecules of water of crystallization at 100° similar to the samarium compound.

Calculated: Nd_2O_3 , 34.17. Found: Nd_2O_3 , 34.24.

Neodymium Ethylsulfonate, $(\text{C}_2\text{H}_5\text{SO}_3)_2\text{Nd}_2 \cdot 6\text{H}_2\text{O}$. — The formation of this compound was brought about in the same manner as the preceding. It appeared to be less soluble than the methylsulfonate however, for it

crystallized easily upon evaporation and being allowed to stand for a short time. The powdered salt was washed with ether. It possessed a pale amethyst color, was insoluble in acetone and ether, soluble in alcohol, and very soluble in water.

Calculated: Nd_2O_3 , 32.02; H_2O , 10.28. Found: Nd_2O_3 , 32.05; H_2O , 9.97.

Neodymium Propylsulfonate, $(\text{C}_3\text{H}_7\text{SO}_3)_6\text{Nd}_2 \cdot 6\text{H}_2\text{O}$.—A solution of this substance gave upon evaporation a voluminous mass of small crystals. They were washed by ether and dried. The propylsulfonate is very soluble in water, soluble in acetone and alcohol. After heating for some time to 100° , one molecule of water remains.

Calculated: Nd_2O_3 , 29.65. Found: Nd_2O_3 , 29.63.

Neodymium Isobutylsulfonate, $(\text{C}_4\text{H}_9\text{SO}_3)_6\text{Nd}_2$.—Crystals of this compound formed with difficulty. They were voluminous, pale amethyst, soluble in alcohol and very soluble in water.

The estimation of Nd_2O_3 gave results corresponding to 8 H_2O , this being one molecule more than the samarium compound possessed. Moisture or efflorescence might be the cause of this difference. However, the salts did not seem to be of sufficient importance to make it worth while preparing again.

Calculated: Nd_2O_3 , 26.81. Found: Nd_2O_3 , 26.94.

Neodymium Ethylene-disulfonate, $(\text{C}_2\text{H}_4(\text{SO}_3)_2)_3\text{Nd}_2 \cdot 10\text{H}_2\text{O}$.—The acid was carefully neutralized with neodymium oxide. The clear solution was evaporated, after which large amethyst crystals formed. They were insoluble in alcohol and acetone, but very soluble in water. When heated to 100° for a long time the salt gradually lost water until a hydrate containing 4 molecules of water remained.

Calculated: Nd_2O_3 , 32.59. Found: Nd_2O_3 , 32.58.

Neodymium Methane-trisulfonate, $(\text{CH}(\text{SO}_3)_3)_2\text{Nd}_2 \cdot 14\text{H}_2\text{O}$.—Fairly large crystals of this substance were obtained by evaporating a solution of the oxide in the corresponding acid. They were of a pale amethyst color, insoluble in alcohol, acetone and acetic acid, but very soluble in water. Like most of the other sulfonates, there was very little difference between the solubilities at room temperature and 100° . This renders these compounds unsuitable for rapid fractionation.

The neodymium trisulfonate, similar to other salts of this acid, is very stable; it is not decomposed by fuming nitric acid, under pressure, until a high temperature is reached.

Calculated: Nd_2O_3 , 32.15. Found: Nd_2O_3 , 32.04.

Neodymium Camphorsulfonate, $(\text{C}_{10}\text{H}_{15}\text{OSO}_3)_6\text{Nd}_2 \cdot 17\text{H}_2\text{O}$.—A solution of this salt obtained in the usual way crystallized with difficulty, yielding a fluffy, very pale amethyst powder, soluble in alcohol and acetone, and very soluble in water.

Calculated: Nd_2O_3 , 16.98. Found: Nd_2O_3 , 17.02.

Several hydrates of the camphorsulfonates appear to exist.

Neodymium 1,3,4-Metaxylenesulfonate, $(C_6H_3(CH_3)_3SO_3)_6Nd_2 \cdot 2H_2O$.—This sulfonate separated out, during the evaporation on a water bath, in crystalline form. It was of a very pale amethyst color, insoluble in acetone, slightly soluble in alcohol and soluble in water.

Calculated: Nd_2O_3 , 22.46. Found: Nd_2O_3 , 22.35.

Neodymium Metasulfobenzoate, $(C_6H_4 \begin{array}{c} \text{SO}_3 \\ \diagup \quad \diagdown \\ \text{COO} \end{array})_6Nd_2 \cdot 9H_2O$, formed pale colored crystals soluble in alcohol and acetone, and very soluble in water.

Calculated: Nd_2O_3 , 32.03. Found: Nd_2O_3 , 32.19.

Neodymium Quinate, $(C_6H_7(OH)_4COO)_6Nd_2 \cdot 11H_2O$.—Neodymium hydroxide was boiled with quinic acid; the solution filtered and evaporated. The quinate crystallized out upon cooling. Pale amethyst colored powder, slightly soluble in cold water.

Calculated: Nd_2O_3 , 20.62. Found: Nd_2O_3 , 20.61.

Neodymium Anisate, $(C_6H_4 \cdot CH_3O \cdot COO)_6Nd_2$.—This compound was precipitated when a slightly acid solution of sodium anisate was added to a nearly neutral solution of neodymium chloride. Free anisic acid was removed from the precipitate by means of hot acetone. The pale colored precipitate was insoluble in water.

Calculated: Nd_2O_3 , 28.16; H, 3.54; C, 48.19. Found: Nd_2O_3 , 28.17; H, 3.31; C, 48.29.

Neodymium Oxanilate, $(C_6H_5NHOCOOCOO)_6Nd_2 \cdot 5H_2O$.—When neodymium chloride was added to a hot, slightly acid solution of sodium oxanilate, a thick sticky mass separated, which rapidly became hard and crystalline upon cooling. The compound was insoluble.

Calculated: Nd_2O_3 , 24.70. Found: Nd_2O_3 , 24.69.

Neodymium Cacodylate, $((CH_3)_2AsO_2)_6Nd_2$.—Cacodylic acid was saturated with neodymium hydroxide. The liquid was filtered and evaporated. Upon cooling, the salt separated in very soft asbestos-like crystals. It was insoluble in alcohol and acetone, slightly soluble in cold water, and soluble in hot water.

Calculated: Nd_2O_3 , 30.31. Found: Nd_2O_3 , 30.40.

Neodymium Hydroxyethanesulfonate.—A solution containing this compound would not crystallize, so as to be workable.

DURHAM, NEW HAMPSHIRE.

A NEW METHOD FOR THE SEPARATION OF THORIUM.

BY T. O. SMITH AND C. JAMES.

Received January 13, 1912.

While working upon the separation of thorium from the rare earths the authors observed that sebacic acid gave a precipitate in a neutral solution which appeared to be quantitative.

Thorium sebacate is a voluminous, granular precipitate which settles

readily and is easily filtered. Solutions of cerium, lanthanum, yttrium, etc., give no precipitate with sebacic acid even upon boiling.

In order to determine whether or not the above observations were correct, the following work was carried out.

A thorium nitrate solution was prepared, carefully standardized by the oxalic acid and hydrogen peroxide methods, and was found to contain 0.005572 gram of thorium dioxide per cc.

The precipitant was used in the form of a boiling solution practically saturated at that temperature.

Fifty cc. portions of the standard thorium nitrate solution were measured into a 250 cc. beaker and raised to the boiling point. A slight excess of the hot solution of sebacic acid was added slowly with continuous stirring. The precipitate which formed at once was immediately filtered and thoroughly washed with boiling water. The sebacate washes readily and the operation may be performed with ease in a very short time. The precipitate was rapidly dried, ignited and weighed as thorium dioxide.

The following data show a good agreement with the standardization by oxalic acid:

No. of cc. of standard thorium solution.	Grams ThO_2 precipitated by oxalic acid.	Grams ThO_2 precipitated by sebacic acid.
50	0.2791	0.2787
50	0.2786	0.2785
50	0.2780	0.2786
50	0.2783	0.2790
50	0.2787	0.2792
50	0.2790	0.2790
Average,		0.2788

The next step was to ascertain the effect of the presence of rare earths upon the thorium precipitate. Accordingly a solution consisting chiefly of cerium, together with fair amounts of lanthanum, praseodymium, neodymium and traces of samarium, gadolinium, etc., was prepared. Varying quantities of this solution which contained 0.005516 gram of the combined oxides per cc. were added to the standard thorium solution. The thorium dioxide was determined as above.

Results are given below:

No. of cc. of standard thorium solution.	Grams of rare earth oxides present.	ThO_2 present by average of oxalic and sebacic standardization.	ThO_2 found.
50	0.05516	0.2787	0.2789
50	0.11032	0.2787	0.2786
50	0.16548	0.2787	0.2789
10	0.5516	0.05574	0.0562
10	0.5516	0.05574	0.0565
10	0.5516	0.05574	0.0564

The authors did not test the action of salts such as dysprosium, erbium, thulium, etc., upon the thorium precipitate, as these elements occur only in small amounts in the ordinary thorium minerals.

Separation of Thorium from the Rare Earths.

The reaction between sebacic acid and neutral thorium solutions would appear to be valuable for the separation and purification of thorium materials.

Sebacic acid can probably be prepared more cheaply than the reagents ordinarily used for the more rapid purification of thorium. It is formed when castor-oil soap is heated with sodium hydroxide. It dissolves in 1000 parts of water at 17° , 40 parts per liter at 65° and at the boiling point becomes fairly soluble. Owing to its slight solubility in cold water it can readily be recovered; hence, it could be used in the separation of thorium on a large scale.

Qualitative Tests with Other Acids.

Phenoxyacetic acid, $\text{CH}_3(\text{OC}_6\text{H}_5)\text{COOH}$, precipitated thorium from a neutral solution almost quantitatively. The addition of aniline did not aid in the separation. It was therefore considered that thorium phenoxyacetate was very slightly soluble in water.

The ortho-nitro-phenoxyacetic acid did not give satisfactory results.

Mucic acid, $(\text{CHOH})_4(\text{COOH})_2$, gave a precipitate which filtered slowly and was not quantitative.

Anisic acid, $\text{C}_6\text{H}_4(\text{OCH}_3)\text{COOH}$, only partially precipitated thorium from a neutral solution.

Aspartic acid, $\begin{array}{c} \text{CH}_2\text{CONH}_2 \\ | \\ \text{CH}_2\text{COOH} \end{array}$, when boiled with a neutral solution of thorium nitrate gave a precipitate which could not be separated by filtration.

Pyrotartaric acid, $\begin{array}{c} \text{CH}_2\text{CHCOOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$.—The addition of this acid to a cold neutral solution of thorium nitrate caused no precipitation. However, upon boiling, a curdy precipitate rapidly formed and after filtering no thorium was found in the solution. From the above facts it would seem that pyrotartaric acid could be used for the quantitative determination of thorium.

Since the cost of pyrotartaric acid is considerably greater than that of sebacic acid, and since the former cannot be regained so readily, no further work was done with it.

Oxanilic acid, $\text{C}_6\text{H}_5\text{NHCOCOOH}$, precipitates both the rare earths and thorium from neutral solutions. From slightly acid solutions thorium

only is precipitated. By increasing the concentration of the acid the precipitate redissolves.

All the above acids, with the exception of oxanilic, give no precipitate with the rare earths in cold or hot neutral solutions.

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NOTES.

A Modification of the Modified Winkler Method for the Determination of Sulphates in Water.—The Modified Winkler Method for the determination of sulphates in water colorimetrically consists in adding to the sample a small amount of barium chromate, acidifying with a few drops of concentrated hydrochloric acid, bringing to a boil, cooling, then adding sodium hydroxide solution (1 : 10) carefully until a tiny drop of the liquid placed upon red litmus paper produces a blue color; a greater excess of alkali must be avoided as the solubility of barium chromate varies greatly with the degree of alkalinity. After filtering, the color is compared in a colorimeter with that of a standard solution of potassium chromate. A correction must be made for the solubility of barium chromate. The SO_4 is equivalent to the CrO_4 found. It is a more or less tedious step in the procedure to neutralize the hydrochloric acid to just the right point. It occurred to the writer to modify the method at this point by changing the acidity from hydrochloric acid to acetic acid by the addition of sodium acetate. This seems to give good results and is easily carried out.

The process as modified is as follows: Measure into an Erlenmeyer flask 150 cc. of the sample. Add 10 drops of concentrated hydrochloric acid and sprinkle in 0.1 to 0.2 g. of pure barium chromate. Rapidly bring the contents of the flask just to a brisk boil. Cool at once and to the cooled liquid add 5 g. of sodium acetate. Filter, transfer 100 cc. of the clear filtrate to a colorimeter cylinder and make alkaline with sodium hydroxide. The standard for comparison should be made slightly stronger than this solution and should be made up to 100 cc. after adding sodium hydroxide to alkaline reaction. A blank determination must be made, using distilled water, to determine the correction to apply for the solubility of the barium chromate under the conditions of the experiment.

It requires but a moment to weigh out the sodium acetate (a close approximation is sufficient). This method gives duplicate results agreeing perfectly within one's ability to read the colors.

The following determinations were made by the method as described.

Different amounts of potassium sulphate were added to separate portions of distilled water and the SO_4 determined.

	Parts per million of SO_4 added.	Found (a).	Found (b).
1.....	27	22	22
2.....	54	53	52
3.....	108	105	104
4.....	In a water sample		SO_4 (parts per million).
Found by author's method.....			101.5
Found by Modified Winkler Method in the hands of another experimenter.....			101
Found by precipitation as BaSO_4			100

The correction applied for the solubility of the barium chromate used, under the conditions of the experiment, was 11 parts of SO_4 per million of water.

HOWARD W. BRUBAKER.

A New Apparatus for Extracting Liquids.—Hitherto all the usual types of apparatus for extraction of liquids have very fragile spirals, are difficult to clean and if a large quantity of liquid is to be extracted, the extraction must be interrupted by changing the liquid.

The following apparatus avoids these disadvantages. This apparatus differs from the usual Soxhlet apparatus for extracting solids only by the inner funnel-tube with a spiral-jacket, the inlet funnel and the higher opening of the siphon.

The use of the apparatus is as follows:

The apparatus is filled with the liquid up to near the siphon. Then by heating the flask filled with ether, etc., the ether vaporizes and the vapor goes through the vapor-tube to the condenser as in the ordinary Soxhlet apparatus. The condensate drops in the inner funnel-tube and rises in small drops following the thread of the funnel-jacket to the surface of the liquid. In this manner very good contact between the ether and the liquid to be extracted is obtained.¹ The ether accumulates above the surface of the liquid until it siphons over and the operation continues. Upon finishing the extraction, which can be ascertained by testing a small portion of the liquid drawn off through the cock, the liquid is removed and a new portion added through the funnel without taking the apparatus apart or interrupting the heating.

The condenser is a new return-condenser with the

¹ F. Friedrichs, "New Gas-washing Bottle," *Z. anal. Chem.*, 50, 175-176; *C. A.*, 5, 1694 (1911).

principle of counter-currents.¹ The essential feature of this condenser is the spiral cooling tube. The condensate between it and the outside-jacket forms a seal, compelling the vapor to travel a spiral distance of 4 feet up through the condenser.² To avoid heating the incoming cooling water by the outgoing warm water the outlet tube is insulated by an air-jacket. This jacket is enlarged so as to make the cooling water also take a spiral course exactly against the vapor.

This apparatus is manufactured by Greiner & Friedrichs, G. m. b. H, Stützerbach, Germany.

Fritz Friedrichs.

ITHACA, N. Y.

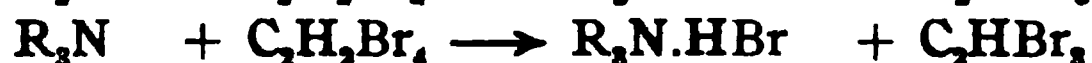
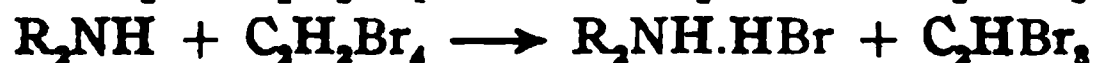
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF TETRABROMETHANE ON ORGANIC BASES.

By WILLIAM M. DEHN.

Received December 18, 1911.

Tetrabromethane (acetylene tetrabromide) reacts with organic bases³ with the greatest ease, yielding products in accordance with the equations:



The reactions were brought about in anhydrous ether, the salts of the respective bases being precipitated and the tribromethylene remaining in the ether solution. It was easily observed that the precipitations of the salts were accelerated by direct sunlight.⁴ Solutions which remained clear in the dark were immediately precipitated by direct sunlight. These reactions were easy and quantitative and afford a convenient method of preparation not only of crystallized salts of the bases but also tribromethylene.⁵

In general aliphatic amines were more easily acted upon by tetrabromethane than the aromatic bases; primary amines were more easily acted upon than the secondary and the tertiary amines. Piperidine was almost instantaneously and quantitatively precipitated as the hydrobromide when treated with tetrabromethane, hence it is the most useful of all the bases to prepare tribromethylene from tetrabromethane.

Preparation of Tribromethylene.—A solution of tetrabromethane in dry ether is treated with piperidine as long as a precipitate forms. The

¹ *Chem. Z.*, 35, 1125 (1911).

² *Z. angew. Chem.*, 23, 2425-26. *C. A.*, 5, 1347 (1911).

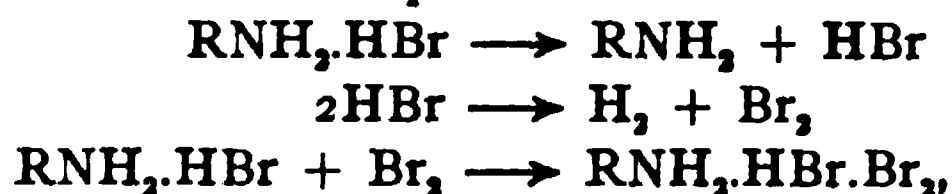
³ Ells and Neuman studied the effect of ammonia, aniline and dimethyl aniline on tetrabromethane in alcoholic solution. They also obtained tribromethylene as the end-product. Ells, Neuman, *J. prakt. Chem.*, [2] 58, 250.

⁴ Compare Dehn and Dewey, *THIS JOURNAL*, 33, 1588.

⁵ See page 287. Also compare Lennox, *Ann.*, 122, 125. Sabanejeu, *Ann.*, 178, 122. Demole *Biol.*, 29, 207. Dworkowitsch, *Ann.*, 216, 280.

filtered ether solution, if alkaline in reaction, is neutralized with dilute hydrochloric acid; the ether solution then is dried with calcium chloride and fractionated. Tribromomethylene, boiling at 163–164°, is obtained in nearly quantitative yields. Since the piperidine is easily recovered from its hydrobromide salt, the method is inexpensive.

In the following experiments nearly quantitative yields of the pure hydrobromides of the bases were obtained. When prepared from the free bases by treatment with aqueous hydrobromic acid, many of these salts are more or less colored and are imperfectly crystallized. The former of these defects results from hydrolysis and decomposition of the salts in accordance with the equations:

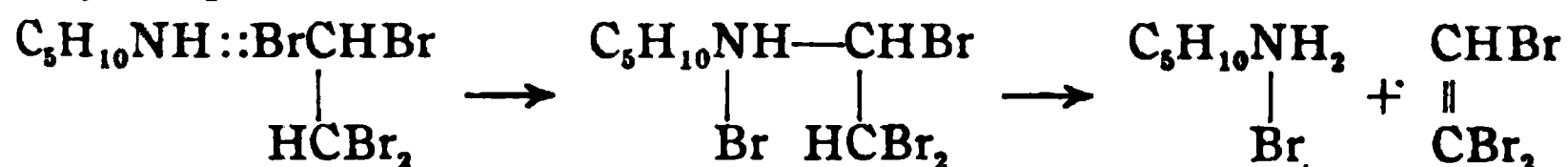


mixtures of the salts with *perbromides* of the salts being formed. Furthermore, imperfectly crystallized forms of the salts are usually obtained, when their aqueous solutions are evaporated, because of the too ready solubility of the salts in water.

Since convenient quantities of pure hydrobromides were obtained in the treatment of the organic bases with tetrabromomethane, their *mercuric bromides* and *bromaurates* were prepared. These latter compounds, derivatives of convenient form to identify the bases, were found invariably to be composed of one molecule of the salt and one molecule of the mercuric bromide or the auric bromide. The mercuric bromides were formed by dissolving equimolecular quantities of the respective salts and mercuric bromide in water and concentrating on the water bath until crystals began to form. If the solutions tended to lose free base by hydrolysis and volatilization, a little aqueous hydrobromic acid was added before evaporating; if too much hydrobromic acid was added, oily precipitates were formed.

The bromaurates were formed by adding to an aqueous solution of the salts a solution of the auric bromide, as long as a precipitate formed. The precipitates were filtered out and recrystallized from water.

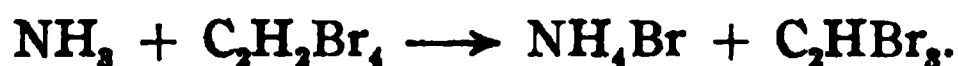
The mechanism of the reaction of organic bases with tetrabromomethane is very simple as indicated below:



Ammonia.—When an anhydrous ether solution of tetrabromomethane was treated with anhydrous ammonia,¹ a slow-forming white precipitate, promoted by direct sunlight, was formed. The precipitate was dried and analyzed. Calculated for NH_4Br ; Br: 81.59; found, 81.59. The ether

¹ Ells and Neuman, *J. prakt. Chem.*, [2] 58, 250.

solution yielded by distillation tribromethylene, therefore, the following reaction took place:



Ethylamine.—When equimolecular quantities of ethylamine and tetrabromethane were brought together in anhydrous ether, an immediate and voluminous white precipitate was formed; the solution warmed almost to the point of boiling. The ether solution yielded by distillation an oil boiling between 163–165°. Calculated for C_2HBr_3 : Br, 90.55; found, 90.66. The precipitate proved to be ethylamine hydrobromide.¹ Calculated for $\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{HBr}$: Br, 62.59; found, 62.72. *Mercuric bromide*, crystals easily soluble in alcohol and water, but insoluble in ether. Melts at 91°. Calculated for $\text{C}_2\text{H}_5\text{NH}_2 \cdot \text{HBr} \cdot \text{HgBr}_2$: Br, 49.55; found, 49.22.

Diethylamine.—Equimolecular quantities of the two substances gave a quantitative yield of tribromethylene and white crystalline *diethylamine hydrobromide*, melting sharply at 205°. Calculated for $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HBr}$: Br, 51.88; found, 51.96. *Bromaurate*, small red needles, quite soluble in water and melting at 162°. Calculated for $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HBr} \cdot \text{AuBr}_3$: Au, 33.37; found, 33.25. *Mercuric bromide*, needles, melting at 120°. Calculated for $(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HBr} \cdot \text{HgBr}_2$: Br, 46.65; found, 46.50.

Triethylamine.—When equimolecular quantities of the two substances were brought together in anhydrous ether the solution remained clear for some time. Later, especially in direct sunlight, flaky crystals of the hydrobromide² separated. Calculated for $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HBr}$: Br, 43.84; found, 43.63. *Bromaurate*, red flaky crystals, melting at 140°. Calculated for $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HBr} \cdot \text{AuBr}_3$: Au, 31.85; found, 32.01. *Mercuric bromide*, beautiful tufts of long white needles, melting at 109°. Calculated for $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HBr} \cdot \text{HgBr}_2$: Br, 44.24; found, 44.18.

Dipropylamine.—An immediate and voluminous precipitate was formed; after two days, beautiful mother-of-pearl leaflets of *dipropylamine hydrobromide*, melting at 271°, were obtained. Calculated for $(\text{C}_3\text{H}_7)_2\text{NH} \cdot \text{HBr}$: Br, 43.89; found, 43.95. *Bromaurate*, fan-like clusters of red needles, melting at 119°. Calculated for $(\text{C}_3\text{H}_7)_2\text{NH} \cdot \text{HBr} \cdot \text{AuBr}_3$: Au, 31.86; found, 31.75. *Mercuric bromide*, long, white needles, melting at 109°. Calculated for $(\text{C}_3\text{H}_7)_2\text{NH} \cdot \text{HBr} \cdot \text{HgBr}_2$: Br, 44.24; found, 44.21.

Tripropylamine.—The solution remained clear in diffused sunlight, and in direct sunlight slowly precipitated *dipropylamine hydrobromide*,

¹ THIS JOURNAL, 33, 1598.

² Garzine gives the melting point at 238–240°, *Jahrb.*, 1889, 1327. The above crystals melted at 236°. Since most of the salts given in this contribution melt with decomposition, the melting points were determined by rapidly heating the substances in sealed capillary tubes.

small white needles, melting at 180° . Calculated for $(C_3H_7)_3N.HBr$: Br, 35.66; found, 35.52. *Bromaurate*, small prismatic needles, difficultly soluble in water and melting at 149° . Calculated for $(C_3H_7)_3N.HBr.AuBr_3$: Au, 29.83; found, 29.75. *Mercuric bromide*, white glistening needles, melting at 104° . Calculated for $(C_3H_7)_3N.HBr.HgBr_2$: Br, 41.05; found, 41.15.

Isobutylamine.—The solution remained clear at first but after a few hours a heavy oily precipitate, which finally became solid, was obtained. *Isobutylaminehydrobromide*, small white flakes, melting at 138° . Calculated for $C_4H_9NH_2.HBr$: Br, 51.82; found, 51.68. *Bromaurate*, needles, easily soluble in water and melting at 154° . Calculated for $C_4H_9NH_2.HBr.AuBr_3$: Au, 33.36; found, 33.41. *Mercuric bromide*, long transparent rectangular plates, melting at 164° . Calculated for $C_4H_9NH_2.HBr.HgBr_2$: Br, 46.63; found, 46.73.

Diisobutylamine.—Precipitates slowly in direct sunlight the *hydrobromide*, pearly flakes, melting at 313° . Calculated for $(C_4H_9)_2NH.HBr$: Br, 38.04; found, 37.96. *Bromaurate*, rectangular plates, melting at 245° . Calculated for $(C_4H_9)_2NH.HBr.AuBr_3$: Au, 30.48; found, 30.35. *Mercuric bromide*, pearly white flakes, melting at 60° . Calculated for $(C_4H_9)_2NH.HBr.HgBr_2$: Br, 42.06; found, 41.87.

Amylamine.—An immediate precipitation of the *hydrobromide*, mother-of-pearl scales, melting at 243° . Calculated for $C_5H_{11}NH_2.HBr$: Br, 47.55; found, 47.43. *Bromaurate*, needles, very soluble in water and melting at 105° . Calculated for $C_5H_{11}NH_2.HBr.AuBr_3$: Au, 32.59; found, 32.40. *Mercuric bromide*, a feathery mass of glistening white plates, melting at 213° . Calculated for $C_5H_{11}NH_2.HBr.HgBr_2$: Br, 45.42; found, 45.19.

Diisoamylamine.—Beautiful mother-of-pearl leaflets of the *hydrobromide*, melting about 315° . Calculated for $(C_5H_{11})_2NH.HBr$: Br, 33.56; found, 33.67. *Bromaurate*, long feathery needles, melting at 220° . Calculated for $(C_5H_{11})_2NH.HBr.AuBr_3$: Au, 29.21; found, 29.16. *Mercuric bromide*, transparent leaflets, melting at 97° . Calculated for $(C_5H_{11})_2NH.HBr.HgBr_2$: Br, 40.10; found, 40.19.

Allylamine.—An immediate though not heavy precipitate; a liquid at first, then a solid. The *hydrobromide*, hygroscopic needles melting at 91° . Calculated for $C_3H_5NH_2.HBr$: Br, 57.97; found, 57.74. *Mercuric bromide*, white flakes, melting at 115° . Calculated for $C_3H_5NH_2.HBr.HgBr_2$: Br, 48.16; found, 48.01.

Benzylamine.—Clear at first, then pearly leaflets of the *hydrobromide*.¹ *Mercuric bromide*, transparent rhombic plates of a soapy feel and melting at 211° . Calculated for $C_7H_7NH_2.HBr.HgBr_2$: Br, 42.51; found, 42.65.

¹ Bischoff, *Ber.*, 30, 3170.

Dibenzylamine.—Mother-of-pearl leaflets of the hydrobromide.¹ *Bromaurate*, orange powder, insoluble in water and melting at 165°. Calculated for $(C_7H_7)_2NH.HBr.AuBr_3$: Au, 27.58; found, 27.41. *Mercuric bromide*, pearly white flakes, melting at 145°. Calculated for $(C_7H_7)_2NH.HBr.HgBr_2$: Br, 37.58; found, 37.41.

Pyridine.—Clear at first; opaque in direct sunlight. The precipitate consisted of red-yellow crystals and a dark colored oil. Crystals, soluble in water, melting² at 212° and forming a bromaurate,³ proved the presence of the hydrobromide. *Mercuric bromide*, rectangular plates and prisms, melting at 152°. Calculated for $C_5H_5N.HBr.HgBr_2$: Br, 46.12; found, 46.17.

Picoline.—At first a clear solution, then a dark colored oil, finally a solid, proving to be the hydrobromide.⁴ *Mercuric bromide*, coarse white needles, melting at 88°. Calculated for $C_6H_7N.HBr.HgBr_2$: Br, 44.91; found, 44.89.

Piperidine.⁵—An immediate and voluminous precipitate of the hydrobromide.⁶ *Mercuric bromide*, transparent hexagonal plates or long needles, melting at 143°. Calculated for $C_5H_{11}N.HBr.HgBr_2$: Br, 45.68; found, 45.71.

Phenylhydrazine.—Glistening white rhombic plates or needles, melting at 188°, the hydrobromide,⁷ $(C_6H_5N_2H_3)_2.HBr$.

The action of tetrachlorethane, tetraiodoethylene, chloropicrin, bromopicrin, tribromophenol, perchlorobenzene, iodoform and other polyhalogenated compounds on organic bases is being investigated.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF TETRAIDOETHYLENE ON ORGANIC BASES.

BY WILLIAM M. DEHN.

Received January 2, 1912.

It was previously shown that carbontetrabromide⁸ and diiodoacetylene⁹ react with organic bases in ether solution to form "carbontetrabromides of crystallization" and "diiodoacetylenes of crystallization," respectively. It is shown herein that tetraiodoethylene unites with organic bases in a similar manner, yielding *tetraiodoethylenes of crystallization*. Usually

¹ Limpricht, *Ann.*, 144, 313.

² Trowbridge, *THIS JOURNAL*, 21, 67. Dehn and Dewey, *Ibid.*, 33, 1596.

³ *Ibid.*, 33, 1596.

⁴ Murrill, *THIS JOURNAL*, 21, 842; *Phil. Mag.*, [5] 2, 271.

⁵ See page 286.

⁶ Bischoff, *Ber.*, 31, 2841. Fock, *Ibid.*, 32, 1409.

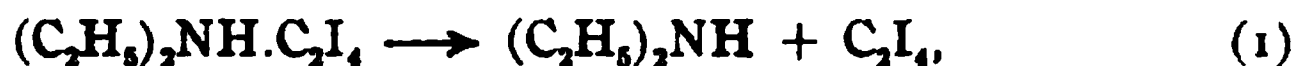
⁷ *Ibid.*, 33, 1597.

⁸ *THIS JOURNAL*, 33, 1588.

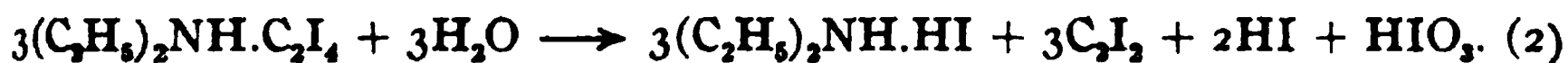
⁹ *Ibid.*, 33, 1598.

one molecule of the base unites with one or two molecules of tetraiodoethylene to form the molecular compound.

Though the bases unite with one or two molecules of tetraiodoethylene, the resulting "molecular compounds" cannot be considered "loosely combined compounds," or compounds closely related to hydrated salts. This conclusion is reached first for the reason that here, as with the carbontetrabromides and the diiodoacetylenes, sunlight is usually necessary to promote the reactions, when the substances are brought together in anhydrous ether. Secondly, the molecular compounds, when decomposed by water, do not smoothly yield the original compounds. For instance, with the diethylamine compound and water, though the main reaction is in accordance with the equation,



the compound also dissociates largely in the following complicated manner:



Though the normal course of reaction of the organic bases on tetraiodoethylene is as indicated above, secondary reactions give rise to deep-colored solutions possessing the odor of diiodoacetylene. These facts are accounted for by the following equations,



periodides being formed and giving rise to the deep-colored solutions. For this and the following described reasons the mass of crystals precipitated from the ether solution is usually a mixture of two or more substances. For instance, with diethylamine, there may be present in the mass $\text{Et}_2\text{NH} \cdot \text{HI}$, $\text{Et}_2\text{NH} \cdot \text{C}_2\text{I}_4$, $\text{Et}_2\text{NH}(\text{C}_2\text{I}_4)_2$, $\text{Et}_2\text{N}(\text{C}_2\text{I}_4)(\text{C}_2\text{I}_2)$, C_2I_4 , the periodides indicated above, C_2I_2 and its derivatives with organic bases.¹ The mixtures thus formed often presented great difficulties in separation. The periodides, tetraiodoethylene and diiodoacetylene are soluble in ether; the two types of compounds of the base with tetraiodoacetylene are insoluble in ether but soluble in chloroform; the salts of the base are insoluble in ether and chloroform but are soluble in alcohol or water; the compounds represented by the type $\text{Et}_2\text{NH} \cdot (\text{C}_2\text{I}_4)(\text{C}_2\text{I}_2)$ are usually insoluble in these organic solvents and with water yield tetraiodoethylene and diiodoacetylene.

The crystals, therefore, are washed with ether and extracted first with chloroform, to separate the tetraiodoacetylenes of the bases; then with absolute alcohol to remove the hydroiodides; the residue is usually a compound of the type $\text{Et}_2\text{NH} \cdot (\text{C}_2\text{I}_4)(\text{C}_2\text{I}_2)$.

The tetraiodoethylene used in these experiments was prepared from

¹ THIS JOURNAL, 33, 1598.

diiodoacetylene¹ by treatment in petroleum ether with iodine in slight excess.² The tetraiodoethylene precipitated as golden scales and after filtering and drying was dissolved in anhydrous ether. A saturated solution of tetraiodoethylene in anhydrous ether at 19° contains 47 g. to the liter. Such an ether solution was used as the basis for the calculation of the quantities used.

The *mercuric iodides* were prepared by adding to the aqueous solutions of the hydroiodides an excess of mercuric iodide and heating to boiling. The solutions were filtered and permitted to stand or spontaneously evaporate until crystals of the double compound separated.

The melting points were made by rapidly heating the substances in sealed capillary tubes.

Ethylamine.—When equimolecular quantities of ethylamine and tetraiodoethylene were mixed in anhydrous ether, small glistening light yellow crystals were formed very slowly in diffused sunlight and very rapidly in direct sunlight. The crystalline mass proved to be a mixture of two substances: The first, easily soluble in chloroform and crystallizing in long, white needles, shrinks at 122° and melts at 133°. Calculated for $C_2H_5NH_2(C_2I_4)_2$: I, 91.60; found, 91.96. The other, insoluble in chloroform and absolute alcohol and crystallizing in transparent rectangular leaflets, melts at 155°. Calculated for $C_2H_5NH_2C_2I_4$: I, 88.03; found, 87.87. Evidently the latter is *ethylaminetetraiodoethylene*; the former, *ethylamine-di-tetraiodoethylene*. These two substances in moist air give off the odor of diiodoacetylene and with water yield a precipitate of tetraiodoethylene and an aqueous solution of *ethylaminehydroiodide*, mother-of-pearl leaflets, easily soluble in alcohol, insoluble in ether and melting at 167°. Calculated for $C_2H_5NH_2.HI$: I, 73.36; found, 73.61. *Mercuric iodide*, coarse glistening light yellow prismatic needles, melting at 136°. Calculated for $C_2H_5NH_2.HI.HgI$: I, 60.74; found, 60.65.

Diethylamine.—When equimolecular quantities of diethylamine and tetraiodoethylene were brought together in ether solution, a slow-forming, buff-colored precipitate was obtained. Sunlight greatly promoted the reaction. After four or five days the substance was separated and washed by decantation and recrystallized from chloroform. Beautiful, transparent, rectangular tablets, darkening at 146° and melting at 158°, were obtained. Calculated for $(C_2H_5)_2NH.C_2I_4$: I, 83.94; found, 83.50. With water *diethylaminetetraiodoethylene* yields a variety of products, as shown in equations (1) and (2) above. When 1.4 g. were subjected to steam distillation for two hours, a residue of 0.88 g. or 63% of tetraiodoethylene was obtained. This indicates that reaction (1) is the more

¹ THIS JOURNAL, 33, 1598.

² Homolka and Stolz, *Ber.*, 18, 2283. Moissan, *Bull. soc. chim.*, [3] 7, 746. Biltz, *Ber.*, 30, 1204; 29, 1411.

abundant. The distillate contained 0.12 g. of diiodoacetylene; the aqueous solution, about 0.10 g. of iodic acid and 0.40 g. of *diethylaminehydroiodide*, plates or needles, easily soluble in chloroform and melting, not sharply, at 165° . Calculated for $(C_2H_5)_2NH.HI$: I, 63.13; found, 63.09. *Mercuric iodide*, long transparent needles melting at 115° . Calculated for $(C_2H_5)_2NH.HI.HgI$: I, 57.14; found, 58.02.

Triethylamine.—The substances reacted slowly in the dark and quickly in direct sunlight. The solid product yielded by recrystallization from chloroform or glacial acetic acid transparent prismatic needles which darken at 120° and melt not sharply at 132° .

Calculated for $(C_2H_5)_3N(C_2I_4)_2$: C, 10.31; H, 1.29; N, 1.20; I, 87.18.

Found: C, 10.70; H, 1.56; N, 1.44; I, 87.29.

Triethylamine-di-tetraiodoethylene is decomposed by water yielding tetraiodoethylene and *triethylaminehydroiodide*, short prismatic needles shrinking at 150° and melting with decomposition at 173° . Calculated for $(C_2H_5)_3N.HI$: I, 55.41; found, 55.25. *Mercuric iodide*, light yellow flakes, melting at 84° . Calculated for $(C_2H_5)_3N.HI.HgI_2$: I, 55.75; found, 55.61.

Isopropylamine.—The mixture yielded in direct sunlight a mass of crystals that clung to the glass with great tenacity. After recrystallizing from chloroform, short transparent prisms were obtained. They became opaque in moist air, and melted sharply at 160° .

Calculated for $C_3H_7NH_2(C_2I_4)(C_2I_4)$: I, 87.67; found, 87.48, 87.70. When distilled with steam, diiodoacetylene was carried over, a precipitate of tetraiodoethylene and an alkaline solution of isopropylaminehydroiodide¹ were obtained.

Dipropylamine.—An immediate white precipitate was obtained in direct sunlight. After a number of days the somewhat yellowish precipitate was separated and recrystallized from chloroform. Glistening white prismatic needles or flakes, softening at 116° and melting at 130° , were obtained.

Calculated for $(C_3H_7)_2NH(C_2I_4)_2$: C, 10.31; H, 1.29; I, 87.19.

Found: C, 10.36; H, 1.55; I, 86.88.

With water, *dipropylamine-di-tetraiodoethylene* yields iodic acid, diiodoacetylene, tetraiodoethylene and *dipropylaminehydroiodide*, pearly white flakes, easily soluble in alcohol, insoluble in ether, softening at 220° and melting with decomposition at 229° . Calculated for $(C_3H_7)_2NH.HI$: I, 55.41; found, 55.12. *Mercuric iodide*, colorless leaflets, melting at 81° . Calculated for $(C_3H_7)_2NH.HI.HgI_2$: I, 55.75; found, 55.63.

Diisoamylamine.—Flakes formed almost immediately in direct sunlight. After recrystallizing from chloroform, needles or plates, darkening at 137° and melting at 150° , were obtained.

Calculated for $(C_5H_{11})_2NH.C_2I_4$: C, 20.90; H, 3.37; N, 2.15.

Found: C, 20.85; H, 3.45; N, 2.03.

¹ Malbot, *Bull. soc. chim.*, [3] 4, 69.

With water *diisoamylaminetetraiodoethylene* forms *diisoamylaminehydroiodide*.¹ *Mercuric iodide*, colorless rhombic or six-sided plates or light yellow flakes, melting at 110°. Calculated for $(C_8H_{11})_2NH.HI.HgI_2:I$, 51.52; found, 50.89.

Benzylamine.—A slow-forming precipitate, accelerated by direct sunlight, was obtained; after recrystallizing from chloroform, long silky needles melting at 115°. Calculated for $C_6H_5CH_2NH_2.C_2I_4:I$, 79.47; found, 79.48. Boiled with water, *benzylaminetetraiodoethylene* yielded *benzylaminehydroiodide*, pearly flakes darkening at 150° and melting at 162°. Calculated for $C_6H_5CH_2NH_2.HI:I$, 54.00; found, 55.96. *Mercuric iodide*, small light yellow, glistening needles or prisms, melting at 134°. Calculated for $C_6H_5CH_2NH_2.HI.HgI_2:I$, 55.28; found, 55.35.

ω-Phenylethylamine.—In direct sunlight transparent prisms were slowly precipitated; they melted not sharply at 160°. The crystalline mass was extracted first with chloroform, then with absolute alcohol and yielded a crystalline residue melting with decomposition at 138°. Calculated for $C_6H_5.C_2H_4NH_2(C_2I_4)(C_2I_2):I$, 81.83; found, 82.14. The portion soluble in alcohol yielded by concentrating, *tetraiodoethylene*, and by treating with ether, pearly flakes of *ω-phenylethylaminehydroiodide* darkening at 245° and melting at 267°. Calculated for $C_6H_5NH_2.HI:I$, 50.97; found, 50.91. *Mercuric iodide*, small yellow compact six-sided prismatic needles, softening at 120° and melting at 131°. Calculated for $C_6H_5NH_2.HI.HgI_2:I$, 54.17; found, 54.02.

Piperidine.—In diffused sunlight only a few crystals formed in five days; in direct sunlight, an immediate and voluminous precipitate was obtained. A number of careful analyses were made of this crystalline mass:

Calculated for $C_5H_{11}N.HI$:	C, 28.17;	H, 5.68;	N, 6.59;	I, 59.59.
Calculated for $C_5H_{11}C_2I_4$:	C, 13.63;	H, 1.80;	N, 2.27;	I, 82.27.
Calculated for $C_5H_{11}N(C_2I_4)_2$:	C, 9.40;	H, 0.96;	N, 1.22;	I, 88.41.
Found:	C, 15.57, 15.58; H, 3.49, 3.30; N, 2.58, 2.84; I, 77.83.			

Evidently the crystalline mass was a mixture of piperidine hydroiodide with the mono- or the di-tetraiodoethylene of piperidine. After recrystallization from chloroform alone or from chloroform by addition of anhydrous ether, white needles melting at 147° were obtained. Calculated for $C_5H_{11}N(C_2I_4)_2:I$, 88.41; found, 88.02. When treated with water and distilled, this *piperidine-di-tetraiodoethylene* yielded an alkaline distillate and *piperidinehydroiodide*, white needles softening at 172°. Calculated for $C_5H_{11}N.HI:I$, 59.59; found, 59.51. *Mercuric iodide*, small glistening white or light yellow needles, melting at 104°. Calculated for $C_5H_{11}N.HI.HgI_2:I$, 57.09; found, 56.56.

Quinoline.—A dark granular precipitate was formed very slowly in

¹ Malbot, *Ann. chim phys.*, [6] 13, 504.

direct sunlight. The crystalline mass gave, by recrystallization from chloroform or from absolute alcohol, needles melting at 132° . Calculated for $C_8H_7N.C_2I_4$: I, 76.84; found, 76.79. With water *quinolinetetraiodoethylene* yields tetraiodoethylene and quinolinehydroiodide.¹

Other Bases.—Pyridine gave a slow-forming, dark-colored precipitate difficultly soluble in chloroform; triphenylphosphine, a white granular sticky precipitate melting at 115° ; triethylstibine, white crystals; paraphenylenediamine, a blue-black precipitate; collidine, an immediate precipitate; picoline, coarse dark crystals. The following substances gave no recognizable reaction-products: PCl_3 , $AsCl_3$, $SbCl_3$, AsI_3 , CH_3AsH_2 .

Acetamide.—Golden rhombic flakes, melting at 175° . Calculated for $CH_3CONH_2.C_2I_4$: I, 85.94; found 85.63. This and other products formed by the action of tetraiodoethylene on organic bases will be investigated.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE FORMATION OF METATHIAZINES FROM THIOUREA.²

BY WILLIAM J. HALB AND HARVEY C. BRILL.

Received January 22, 1912.

In a recent publication³ the condensation of urea with nitromalonic aldehyde was shown to give a nitrohydroxypyrimidine as a final product. A comparison of this reaction with condensations where an amino-imino grouping about a central carbon atom could be brought into reaction with this same aldehyde led to the conclusion that this latter grouping was far more reactive in the formation of pyrimidines than the β -diamino grouping in urea.

When thiourea is substituted for urea in this connection, we naturally were led to expect a pyrimidine containing a mercapto group as a substituent in place of the hydroxyl group of that product obtained from urea. The condensation, however, has been found to proceed in a totally different manner.

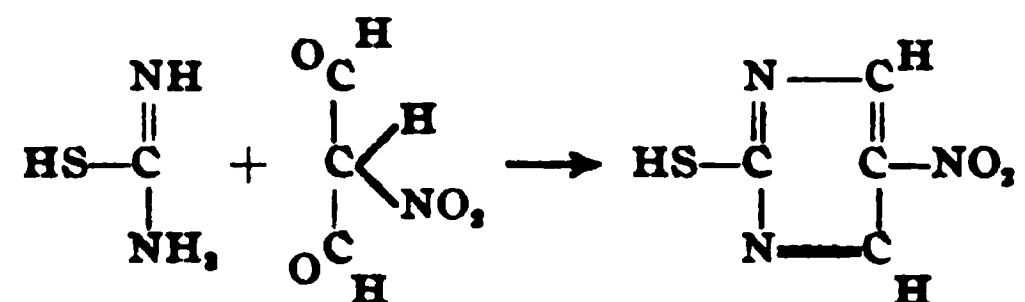
It is well known that thiourea may exist in two isomeric forms, the normal and the pseudo. Granting that the presence of the two amino groups in the normal form ($S : C : (NH_2)_2$) does not offer the favorable configuration which the amino-imino grouping of the pseudo form ($HS.C(:NH)NH_2$) has been found to give for pyrimidine formation, it would follow that we should have from this pseudo form a direct and

¹ Trowbridge, *THIS JOURNAL*, 21, 67.

² The work described in this article formed part of a thesis presented to the Faculty of the Department of Literature, Science and the Arts of the University of Michigan for the degree of Doctor of Philosophy, by Harvey C. Brill.

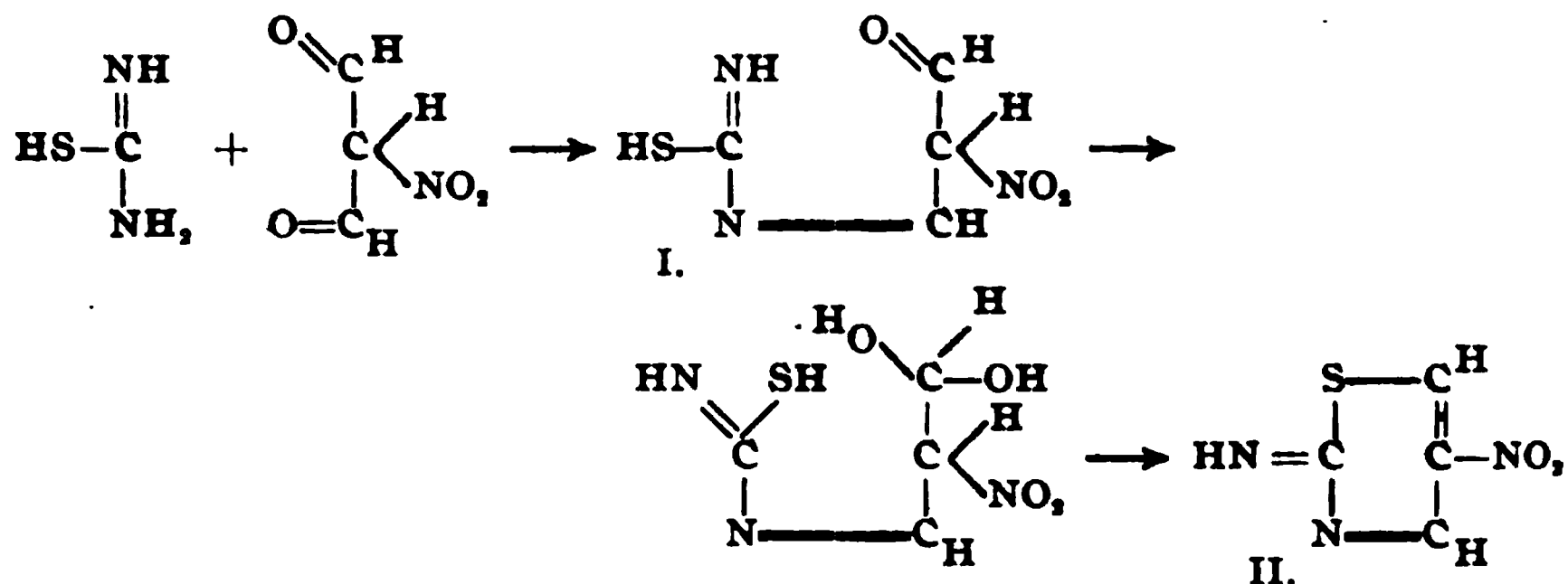
³ *THIS JOURNAL*, 34, 82 (1912).

simple condensation with nitromalonic aldehyde to give a nitromercapto-pyrimidine. The reaction may be indicated as follows:



This type of compound, however, is not produced, but in its stead a compound containing the sulfur atom in the ring. In other words when the amino group of pseudothiurea has condensed with one aldehyde group of nitromalonic aldehyde the second aldehyde group, in hydrated form, enters preferably into reaction with the mercapto group of the thiourea rather than with the imino group. This latter group was indeed found most reactive toward the formation of pyrimidines from amidines. And in this case, as one may expect, we have a condensation which runs just as readily and with good yield.

The compound obtained is in structure a six-membered ring containing one nitrogen atom meta to a sulfur, namely, a metathiazine. The intermediate product has been shown to be a monothioureide of nitromalonic aldehyde (I) as indicated below:



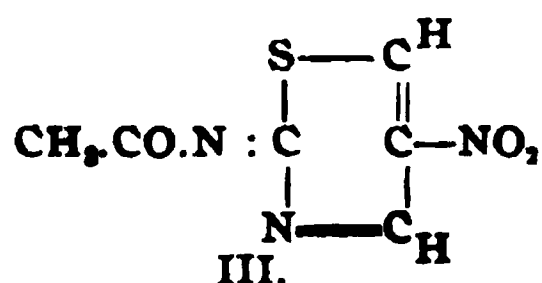
When thiourea and nitromalonic aldehyde are brought together in aqueous solution in the presence of a very small quantity of sodium hydroxide or diethylamine, the condensation proceeds only to the formation of the monothioureide, a yellow semi-crystalline substance removed by acidification of the reaction mixture. When piperidine is employed as the condensing agent the reaction proceeds further with the production of a large quantity of metathiazine, which comes out in a mass of yellow needles. The mother liquor, however, from these crystals still retains a small quantity of the thioureide, which can be removed as before stated by acidification. Condensation in presence of acids gives no well defined product, owing to the decomposition which nitromalonic aldehyde is prone to undergo.

The monothioureide of nitromalonic aldehyde is shown to have but one aldehyde group, since with phenylhydrazine it gave a monophenylhydrazone. When the monothioureide is suspended in alcohol and piperidine added, the substance slowly dissolves and undergoes a transformation into the metathiazine which precipitates immediately. There remains no doubt as to the structure of the monothioureide and its intermediate position in the formation of the metathiazine (II).

The quantity of piperidine here employed as a condensing agent has considerable to do with the yield of metathiazine. There is no combination, however, between piperidine and the final product. The metathiazine is not soluble in alkali. On continued heating with sodium hydroxide solution decomposition slowly takes place and the presence of nitromalonic aldehyde may be detected in certain cases. Upon warming this metathiazine with a basic lead acetate solution, or with mercuric oxide, no desulfurization was accomplished, thus showing the stability of the compound and the ring position of the sulfur.

When the monothioureide was subjected to treatment with basic lead acetate solution or mercuric oxide, desulfurization ensued immediately as may well be expected. The presence of the free imino group in this monothioureide was qualitatively shown by the reaction with benzene sulfochloride (Hinsberg's test) which gave the characteristic oily mass.

The presence of the imino group as a substituent in the metathiazine compound was also shown by the formation of a characteristic oily substance upon the addition of benzene sulfochloride. By action of acetic anhydride only a mono acetyl derivative of this metathiazine could be obtained. This at once proves the presence of only one replaceable hydrogen atom, basic in nature, and confirms also the structure already assigned. The compound formed is, therefore, a β -nitro- μ -acetylimino-metathiazine (III):



The structure of the monothioureide is further substantiated by the fact that a sulfoether is readily prepared from it by the action of dimethyl sulfate. A number of salts were also prepared. The potassium salt indicates three replaceable hydrogen atoms per molecule of monothioureide.

Thiourea has thus been found to condense in its pseudo form with a β -dialdehyde. Similar condensations, in which pseudomethyl- and pseudoethyl-thiourea were employed, have been investigated by Wheeler and

Merriam.¹ The first step in the condensation with thiourea led to a monothioureide, also shown to exist in its pseudo form. Consequently we may conclude that the presence of the imino group in this intermediate product is indicative of the manner in which these condensations must run—namely, first, by condensation between aldehyde and amino group, and second, in formation of ring, by loss of water between the mercapto and one hydroxyl group of the hydrated aldehyde.

Experimental Part.

Monothioureide of Nitromalonic Aldehyde, $C_4H_5O_3N_3S$.—Equimolecular quantities of sodium nitromalonic aldehyde and thiourea were brought together in aqueous solution and a few drops of diethylamine added. The solution (which should be somewhat concentrated) soon acquired a deep red color. After 24 hours the reaction-mixture was just acidified with dilute sulfuric acid and the yellow flocculent precipitate filtered off. This same product may be obtained when sodium hydroxide is used as the condensing agent but in poorer yields. The yield in the case just described is very good. Quantitative results are precluded by reason of decomposition products and then again by the solubility of the thioureide in slightly acid solutions. The purification of this monothioureide is accomplished by crystallization from glacial acetic acid. When carefully carried out the product separates in beautiful glistening yellow leaflets melting at $206-7^\circ$ (cor.). It is soluble in acetic acid; slightly soluble in alcohol, acetone or acetic ester; insoluble in water, benzene, carbon disulfide, ether or ligroin. Its alkaline solution is readily desulfurized by gentle warming with either lead acetate or mercuric oxide.

0.1400 gram substance; 0.1420 gram CO_2 ; 0.0441 gram H_2O . 0.0776 gram substance; 17.22 cc. moist N (23° and 740 mm.). 0.3112 gram substance; 0.4094 gram $BaSO_4$.

Calculated for $C_4H_5O_3N_3S$: C, 27.42; H, 2.88; N, 24.01; S, 18.31.

Found: C, 27.67; H, 3.52; N, 24.22; S, 18.06.

The sulfur in this compound was determined by the sodium peroxide method.

Potassium Salt of Monothioureide of Nitromalonic Aldehyde, $C_4H_5O_3N_3SK_3$.—This salt was prepared by adding to an aqueous suspension of thioureide just sufficient potassium hydroxide solution (1:5) for complete neutralization. From the deep red solution thus formed the long, flat, reddish brown crystals of the potassium salt separated upon spontaneous evaporation. The air-dried salt contains no water of crystallization.

0.3090 gram dried salt; 0.2815 gram K_2SO_4 . Calculated for $C_4H_5O_3N_3SK_3$: K, 40.63; found, 40.89.

This would indicate that not only the mercapto and the isonitroso groups but also the imino group suffered a replacement of hydrogen for potas-

¹ *Am. Chem. J.*, 29, 478 (1903).

sium. A lead salt of this monothioureide was also prepared by careful action of lead acetate upon a solution of the potassium salt. Its analysis, however, was vitiated owing to the great ease with which lead sulfide split off from the molecule.

Methyl Ether of Monothioureide of Nitromalonic Aldehyde, $C_4H_4O_3N_2SCH_3$.—The action of methyl iodide upon the sodium or potassium salt of the monoureide suspended in alcohol met with little success, as only a very small yield of ether could be obtained. When, however, an aqueous solution of the potassium salt is shaken with dimethylsulfate, the methyl ether of the monothioureide is thrown out from the comparatively cold solution in a few minutes. The formation of this flocculent precipitate of the methyl ether is accompanied also by the disagreeable mercaptan odor. It is purified by crystallization from ether, from which it separates in yellow plate-like crystals m. $78-9^\circ$ (cor.). It is soluble in benzene, ether or alcohol, but insoluble in water. It is fairly stable, melting and remelting at 78° .

0.0648 gram substance; 14.05 cc. moist nitrogen (24° and 720 mm.). Calculated for $C_4H_4O_3N_2S$: N, 22.21; found, 22.50.

This methyl ether is not desulfurized by action of basic lead acetate solution.

When the monothioureide and phenylhydrazine acetate are brought together in alcoholic solution the monophenylhydrazone of this monothioureide is formed. The product may be removed by the addition of water to the deep red alcoholic solution, but owing to its noncrystalline character complete purification was not effected.

β -Nitroiminometathiazine, $C_4H_3O_2N_2S$.—Equimolecular quantities of thiourea and sodium nitromalonic aldehyde were brought together in somewhat concentrated aqueous solution and a few drops of piperidine added as a condensing agent. The solution took on a deep red color immediately, and in the course of an hour long, slender, yellow needles of the metathiazine made their appearance. The reaction may be considered at an end in 24 hours. After removal of the product the alkaline mother liquor was just acidified with dilute acid, upon which a fair amount of the yellow monothioureide of nitromalonic aldehyde was precipitated. This mother liquor left after the removal of the metathiazine compound has constituted the principal source of the monothioureide for the present work.

β -Nitroiminometathiazine crystallizes from alcohol in beautiful, long, yellow needles m. $151-2^\circ$ (cor.). It is readily soluble in acetone or benzene; fairly soluble in alcohol, acetic acid or acetic ester; only slightly soluble in water.

Calculated for $C_4H_3O_2N_2S$: C, 30.35; H, 1.91; N, 26.57; S, 20.27.

Found: C, 30.21; H, 2.34; N, 26.90; S, 20.35.

This thiazine is very stable towards both acids and alkalies. It may be crystallized from hot, concentrated hydrochloric acid without decomposition. Prolonged boiling with concentrated alkali slowly breaks up the molecule. A boiling alkaline solution of lead acetate or mercuric oxide is without effect upon it, thus indicating the firmness with which the sulfur is held in the ring. Phenylhydrazine and aniline do not react with the compound, as may be expected now that the free aldehyde group of the monothioureide has become involved with the mercapto group in a ring closing. The action of benzenesulfochloride upon the thiazine gave, upon warming, a yellow oily mass which confirms the presence of the imino group (Hinsberg's test).

β -Nitroacetylminometathiazine, $C_4H_2O_2N_2S(COCH_3)$.—The β -nitroiminometathiazine was warmed with an excess of acetic anhydride for an hour at a temperature of about 50° and the solution then poured into cold water. An oil is first precipitated; this, however, by stirring and a few minutes' standing, passed over into a yellow, semi-crystalline precipitate. The product was purified by crystallization from alcohol and melted at 141° (cor.). It is readily soluble in alcohol, acetone, benzene, acetic ester or carbon tetrachloride; fairly soluble in ligroin or acetic acid; slightly soluble in water, but insoluble in ether.

Calculated for $C_4H_2O_2N_2S$: N, 21.10; S, 16.42; found, 21.24, 16.11.

This acetylminometathiazine is a fairly stable compound. It is easily hydrolyzed, however, by boiling water and yields again the free metathiazine. The production of only a monoacetyl derivative is in exact accord with the structure of the metathiazine as already shown.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE NEVADA AGRICULTURAL EXPERIMENT STATION.]

ALFALFONE, A KETONE OF THE FORMULA $C_{21}H_{42}O$, OBTAINED FROM ALFALFA. ALFALFA INVESTIGATION. II.

BY C. A. JACOBSON.

Received January 13, 1912.

When air-dried alfalfa meal is extracted with hot, 95% alcohol, and the extract allowed to cool, a heavy green precipitate settles out. By filtering, drying and extracting this precipitate with ether, according to the method given in my preliminary paper,¹ a light, fluffy powder results, which serves as the starting point for the present investigation.

About 0.5 gram of this powder together with 150 cc. nitric acid of 1.104 sp. gr. are put into a flask, connected with a reflux condenser and heated on the water bath for about two working days, or until the oily globule floating on top of the acid becomes perfectly transparent. Upon cooling the solution to the room temperature, the globule solidifies into

¹ THIS JOURNAL, 33, 2048.

a waxy-looking cake. The nitric acid solution is found to contain considerable quantities of oxalic acid. After pulverizing and washing the cake free from nitric acid, it is extracted with boiling acetone. The acetone solution is filtered hot, and set aside to cool, when a voluminous white precipitate appears. This precipitate is myristone and has been described in the paper to which reference has already been made.

The hot acetone, however, does not dissolve all of the powder from the oxidized fatty cake, but leaves the greater portion undissolved. This white, amorphous powder is a ketone of the formula $C_{21}H_{42}O$, which I have chosen to call alfalfone, since it has been obtained for the first time from alfalfa.

Alfalfone is insoluble in water, hot and cold acetone and ether, insoluble in cold alcohol but dissolves slightly when this solvent is heated to boiling. Chloroform and carbon disulphide dissolve it to some extent in the cold but easily on warming. A mixture of 90% absolute alcohol and 10% amyl alcohol dissolves alfalfone readily when hot, but precipitates it again on cooling. The same is true of a mixture of 90% petroleum ether and 10% amyl alcohol. Both of these mixtures were employed in the purification of the substance, but it was found that the melting points of the products obtained from the former solvent mixture varied somewhat with different lots and were generally lower than the melting points of the lots obtained by using the petroleum ether mixture. Two lots reprecipitated from the latter solvent mixture gave identical melting points, namely 88.5–88.8°.

Alfalfone manifests the same electrical properties as the myristone with which it is associated in alfalfa. It gives negative tests with bromine for unsaturation, with ferric chloride and alkali for phenolic character, and with acetic anhydride for hydroxyl. It does not give the characteristic color reactions for the cholesterol group. Its chloroform solution does not show any absorption bands either in the visible or ultraviolet part of the spectrum. It is neutral to litmus and phenolphthalein.

Continuous extraction of alfalfa for several months was necessary before enough of this material could be obtained to work with, as the yield is only a small fraction of one per cent. Four different lots of the unoxidized mother substance were heated with nitric acid according to the method given, separated from myristone by boiling acetone and reprecipitated two to three times from a mixture of 90% petroleum ether and 10% amyl alcohol. The resulting substances were then filtered, washed with the same solvent mixture, and dried first in the air, and then in vacuum desiccators over sulphuric acid.

These substances were burned in a Liebig furnace, giving the following results:

	Ia.	Ib.	II.	III.	IVa.	IVb.	Average.
Sub.	0.1524	0.2204	0.1816	0.1696	0.1980	0.1727	...
CO ₂	0.4559	0.6568	0.5395	0.5038	0.5893	0.5157	...
H ₂ O	0.1835	0.2663	0.2197	0.2018	0.2411	0.2067	...
C.	81.56	81.27	81.02	81.02	81.18	81.47	81.32
H.	13.47	13.52	13.54	13.31	13.63	13.40	13.51

Calculated for C₂₁H₄₂O: C, 81.20; H, 13.64.

Like myristone, this ketone did not yield an acid (at least not to any appreciable extent) when oxidized with a chromic-sulfuric acid mixture, but when it was heated with a large excess of sodium in 95% alcohol, the corresponding carbinol was obtained whose properties differ somewhat from the mother substance.

Alfalfone-carbinol is soluble in boiling acetone but settles out when the solution cools. It is more soluble in hot alcohol than the ketone. Both chloroform and amyl alcohol dissolve it at the room temperature. It goes into colloidal solution in carbon disulfide, which at once clears when the temperature is slightly raised.

The carbinol was purified by reprecipitating from hot acetone, washed and dried in a vacuum desiccator. It is a pure white, amorphous powder, with a melting point of 86.3–86.5°.

Following are the results obtained from combustions of two different lots of the carbinol:

Substance, 0.1540, 0.1859; CO₂, 0.4557, 0.5499; H₂O, 0.1928, 0.2254.

Calculated for C₂₁H₄₄O: C, 80.68 ; H, 14.20.

Found: C, 80.68, 80.68; H, 14.01 (13.57).

Not enough material was available for determining the location of the carbonyl group in the ketone or the hydroxyl in the carbinol. The cetyl ether of α -hydroxy- β -methyl butane described by Guye and Chavanne¹ has the same percentage composition as alfalfone-carbinol, but that they are different substances is seen from the fact that the former has a melting point of only 14°. Isoamylcetyl ether² is also isomeric with it, but since its melting point is 30° and that of the carbinol from alfalfone 86.3–86.5°, the two substances must be fundamentally different.

As the work progresses, more and more of this material will accumulate, and it is hoped that enough can be obtained so that the constitutional formula can be ascribed to this new ketone obtained from alfalfa.

¹ *Bull. soc. chim.*, [3] 15, 304.

² *Ann.*, 102, 220.

[OFFICE OF DRUG-PLANT, POISONOUS-PLANT, PHYSIOLOGICAL, AND FERMENTATION INVESTIGATIONS.]

THE MEASUREMENT OF THE OXIDASE CONTENT OF PLANT JUICES.¹

BY HERBERT H. BUNZEL.

Received January 11, 1912.

Introduction.

The importance of the presence of oxidizing enzymes in plants is becoming more and more evident. The work of Palladin² and of others strongly emphasizes their fundamental role in the respiration of plants. The work of Woods³ in this Bureau bears out their significance in diseases of plants. Furthermore their causal relationship to color production in plants,⁴ their important part in the darkening of tea,⁵ as well as in that of bread during its making⁶ and in the production of the smooth black and hard lacquer of the Japanese from the white fluid soft secretion of the tree *Rhus vernicifera*⁷ is well established.

¹ By permission of the Secretary of Agriculture. Communicated at the summer meeting of the American Chemical Society at San Francisco, 1910, and at the winter meeting of the same society at Minneapolis, 1910.

² Palladin, W., "Bildung der verschiedenen Atmungsenzyme in Abhängigkeit von dem Entwicklungs-stadium der Pflanzen," *Ber. Bot. Ges.*, 24, 97-107 (1906). "Die Arbeit der Atmungsenzyme der Pflanzen unter verschiedenen Verhältnissen," *Z. physiol. Chem.*, 47, 406-451 (1906). "Über die Wirkung von Giften auf die Atmung lebender und abgetöteter Pflanzen, sowie auf Atmungsenzyme," *Jahrbücher Wiss. Botanik*, 47, 431-461 (1910).

³ "The Destruction of Chlorophyll by Oxidizing Enzymes," *Centralbl. Bakteriologie*, 5, 745-754 (1899). "Observations on the Mosaic Disease of Tobacco," U. S. Dept. of Agr., Bureau of Plant Ind., *Bull.* 18, 17-22 (1902).

⁴ Agulhon, H., "Influence de la réaction du milieu sur la formation des mélanines par oxydation diastasique," *Compt. rend.*, 150, 1066-68 (1910). Palladin, W., "Synergien, das Prochromogen des Atmungspigmentes der Weizenkeime," *Biochem. Z.*, 27, 442-449 (1910). "Die Verbreitung der Atmungschromogene bei den Pflanzen," *Ber. Bot. Ges.*, 26a, 378-389 (1908). Bourquelot, E., and Bertrand, G., "Le bleuissement et le noircissement des champignons," *Compt. rend. soc. biol.*, [10] 2, 582-584 (1895). Bailey, I. W., "Oxidizing Enzymes and Their Relation to 'Sap-stain' in Lumber," *Bot. Gaz.*, 50, 142-147 (1910). Bourquelot, E., and Fichtenholz, A., "Nouvelles recherches sur la glucoside du poirier, son rôle dans la production des teintes automnales des feuilles," *Compt. rend. soc. biol.*, 69, 605-607 (1910). Combes, R., "Du rôle de l'oxygène dans la formation et la destruction des pigments rouges anthocyaniques chez les végétaux," *Compt. rend.*, 150, 1186-1189 (1910).

⁵ Aso, K., "On the Role of Oxydase in the Preparation of Commercial Tea," *Bull. Coll. Agr. Tokyo*, 4, 255-259 (1901).

⁶ Boutroux, L., "Le pain et la panification," Paris, 1897, p. 184. Bertrand, G., and Mutermilch, W., "Sur la Tyrosinase du son de Froment," *Bull. soc. chim.* [4] 1, 837-841 (1907).

⁷ Bertrand, G., "Sur le latex de l'arbre à laque," *Compt. rend.*, 118, 1215-1218 (1894). "Recherches sur le latex de l'arbre à laque du Tonkin," *Bull. soc. chim.*, [3] 11, 717-721 (1894).

These are only a few examples selected from the extensive literature on the subject,¹ but they fully demonstrate the great need of careful and thorough studies of this class of substances.

Nearly all of the experiments attempting to correlate the oxidase content with biological processes in plants have been of a qualitative nature.

The time has now come when mere qualitative study of enzymes is inadequate. This became particularly evident in the course of some biochemical investigations upon certain pathological conditions of important agricultural crops undertaken in this laboratory in coöperation with other divisions of the Bureau of Plant Industry. Among these conditions were the mosaic disease of tobacco, the curly-top of beets, and diseases of cabbage and spinach on the truck farms of Norfolk. For the first of these Woods² long ago demonstrated changes in the oxidase mechanism. Work in this laboratory has raised the question whether the other conditions mentioned may not also present symptoms of this general type. It was found impossible to settle this question without determining the oxidizing power of these tissues and extracts quantitatively. Unfortunately no sufficiently accurate quantitative methods suitable for the purpose exist. It therefore became necessary to devise such. This task has been undertaken by the writer, and the present report is the first step in the solution of this problem.

The various methods, which in the past have been used in investigations of this sort, are briefly reviewed in an article by Foà³ and are discussed in detail in *Bulletin 238*, Bureau of Plant Industry, Department of Agriculture. In addition to the criticisms made by Foà there are many other, at least as serious objections, to the use of colorimetric methods in the measurement of oxidizing enzymes. In the first place the tissue extracts available are rarely clear and colorless, but generally grayish and turbid, due among other things to the partial oxidation and subsequent precipitation of the chromogens contained in them. Since artificially prepared color standards are free from colored suspended

¹ Issajew, W., "Über die Malzoxydase," *Z. physiol. Chem.*, 45, 331-350 (1905). Kelley, W. P., "The Influence of Manganese on the Growth of Pineapples," Hawaii Agr. Exp. Station, *Press Bull.* 23, 14, Honolulu, 1909. Lagatu, H., "Sur la casse des vins; interprétation nouvelle basée sur le rôle du fer," *Compt. rend.*, 124, 1461-1462 (1897). Bouffard, A., and Semichon, L., "Contribution à l'étude de l'oxydase des raisins. Son utilité dans la vinification," *Compt. rend.*, 126, 423-426 (1898). Caze-neuve, P., "Sur le ferment soluble oxydant de la casse des vins," *Compt. rend.*, 124, 406-408 (1897). Lépinois, E., "Note sur les ferments oxydant de l'aconit et de la belladone," *J. pharm. et chim.*, [6] 9, 49-52 (1899). Lindet, L., "Sur l'oxydation du tannin de la pomme à cidre," *Bull. soc. chim.*, [3] 13, 277-279 (1895).

² Woods, A. F., *loc. cit.*

³ "Eine Methode graphischer Registrierung einiger Gährvorgänge," *Biochem. Z.*, 11, 382-399 (1908).

matter, the comparison becomes very difficult and at the best inaccurate. On the other hand if the oxidase-containing solutions are freed from such disturbing constituents, or if only very small amounts of the juice to be studied are used, the methods based on color comparison become very unreliable. What is badly needed is a method applicable to the juice or extract freshly prepared from the plant tissue, the accuracy of which will be enhanced rather than impaired by the use of larger amounts of material. Fresh plant juices always contain appreciable amounts of protein in solution. It is well known that all proteins, being amphoteric colloids, are capable of combining with or absorbing colored compounds of all sorts. Since in the manipulations referred to in connection with the methods mentioned above no more than a small amount of the colored substance is formed,¹ an appreciable error is introduced whenever fresh tissue juice is used, especially since the protein-dye combination is frequently insoluble.

Methods based on the measurement of the quantity of precipitate produced in the course of the oxidation of water-soluble substances to insoluble compounds are more reliable, but very limited in their applicability. Fürth and Jerusalem¹ measured the tyrosinase content of mushrooms by the volume of the melanin precipitate produced. The method of Bach and Chodat² which is based on the weighing of the purpurogallin formed in the presence of hydrogen peroxide and peroxidase is so well known that it does not require description. The first method here mentioned is inaccurate, the second tedious, owing to the number of weighings, and neither is of general applicability.

As Foà points out, the methods most satisfactory for the measurement of the rate of reactions involving oxygen absorption are those in which the quantities of oxygen absorbed are determined by measuring the changes of pressure within the reaction flask. The present publication deals with the description of such a method.

A manometric method has been devised and used successfully by A. P. Mathews in his work on the spontaneous oxidation of the cell constituents.³ Similar methods have also been used by many other observers for the sake of obtaining a measure of the respiratory enzymes present, but none have observed all of the precautions necessary in such measurements. The precautions to be observed as well as the drawbacks of all methods of this type are described in detail in the bulletin.

¹ "Zur Kenntnis der melanotischen Pigmente und der fermentativen Melaninbildung," *Beitr. chem. Physiol. Path.*, 10, 131-173 (1907).

² Chodat, R., "Darstellung von Oxydasen und Katalasen tierischer und pflanzlicher Herkunft. Methoden ihrer Anwendung." Abderhalden, E., "Handbuch der Biochemischen Arbeitsmethoden," Berlin, 1910, Vol. III, Pt. 1, pp. 42-74.

³ *J. Biol. Chem.*, 6, 3-20 (1909). Mathews, A. P., and Walker, Sidney, *J. Biol. Chem.*, 6, 29-37 (1909).

In most of the experiments described in this paper, potatoes furnished the oxidase preparations. These were used for a number of reasons. They are easily obtainable at all times of the year, and can be readily grown for experimental purposes if it is found desirable to study the variation of oxidase content with varying conditions. Numerous experiments by other observers show that they are rich in oxidases. They seemed therefore the best test object for elaborating the method.

The potatoes used were rinsed off with cold water, and wiped dry with a clean towel. They were peeled, and the peelings ground up in a meat chopper. The juice was obtained by pressing the pulp through a piece of silk cloth. In all the experiments only fresh juice was used. The juice of beet leaves was obtained by pressing it from the cleansed leaves after grinding them in a meat chopper. Neither the potato nor the beet juice was filtered through paper. Since the activity of the juice undoubtedly depends to some extent on the mode of preparation, a method will be devised in the near future by which uniformity in this process can be assured.

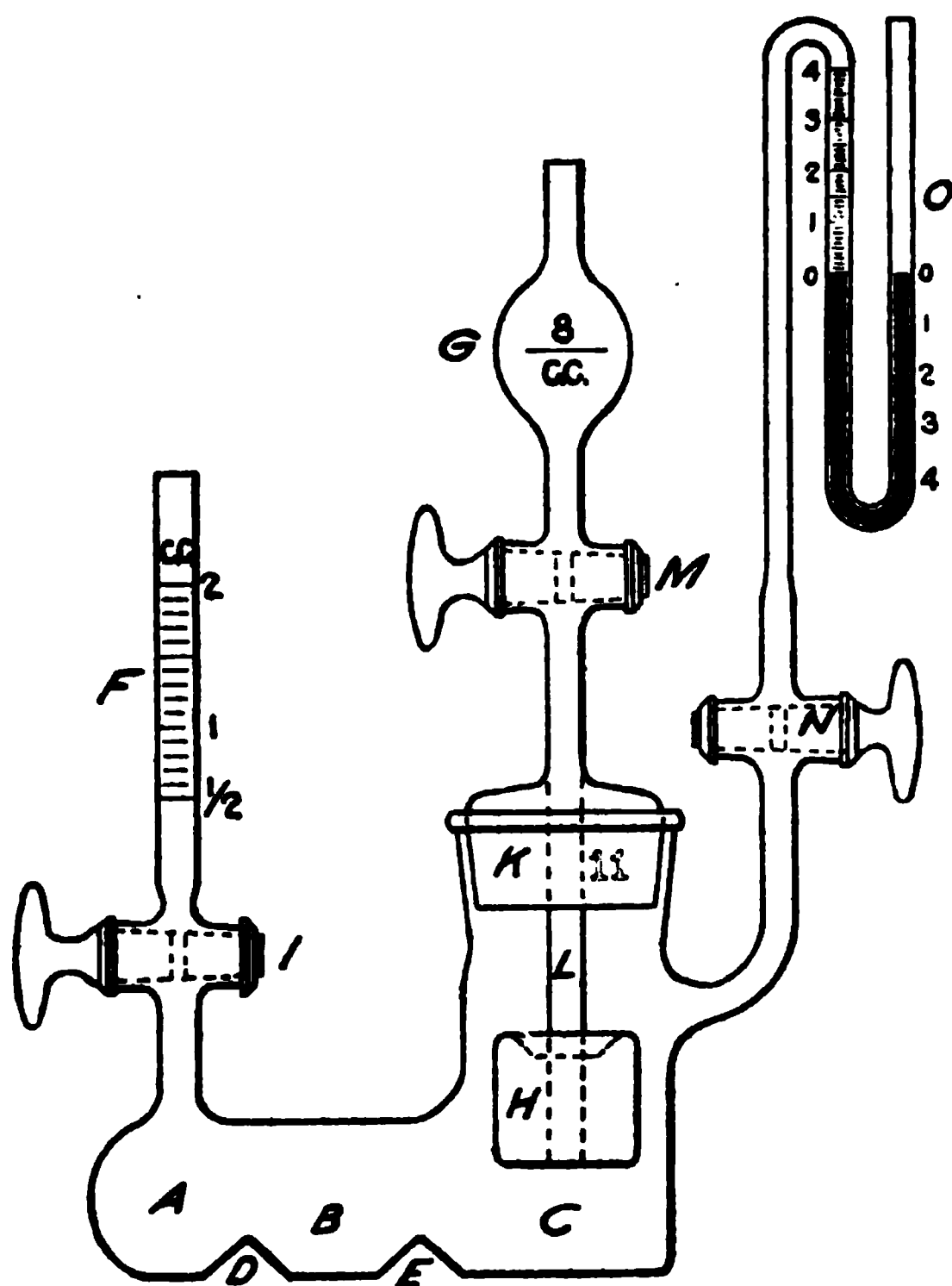


Fig. 1.

To start with it was decided to use pyrogallol as the substance to be oxidized.

It is obvious that all the experiments have to be carried out at a constant temperature. For this purpose an air thermostat was constructed by means of which the temperature could be maintained constant within $0.1-0.2^{\circ}$. A shaking machine was also made especially for the purpose.¹

The procedure of the actual measurement is as follows: The oxidase apparatus (Fig. 1) is clamped on the carriage of the shaking machine in the thermostat.¹ Eight cc. of fresh 1% pyrogallol solution are measured into compartment C by means of bulb G. Two cc. of plant juice are measured into compartment A from buret F. Basket H is charged with 1 cc. normal sodium hydroxide solution. Only stopcock I is left closed. Then the interior of the thermostat is heated to the temperature desired and maintained there. About 30 minutes after the temperature of experimentation is reached, the windows of the thermostat are opened enough to allow the introduction of the arm and the stopcock M closed. Now the shaking machine is brought into action at an approximate rate of 5 complete excursions in 3.3 seconds.

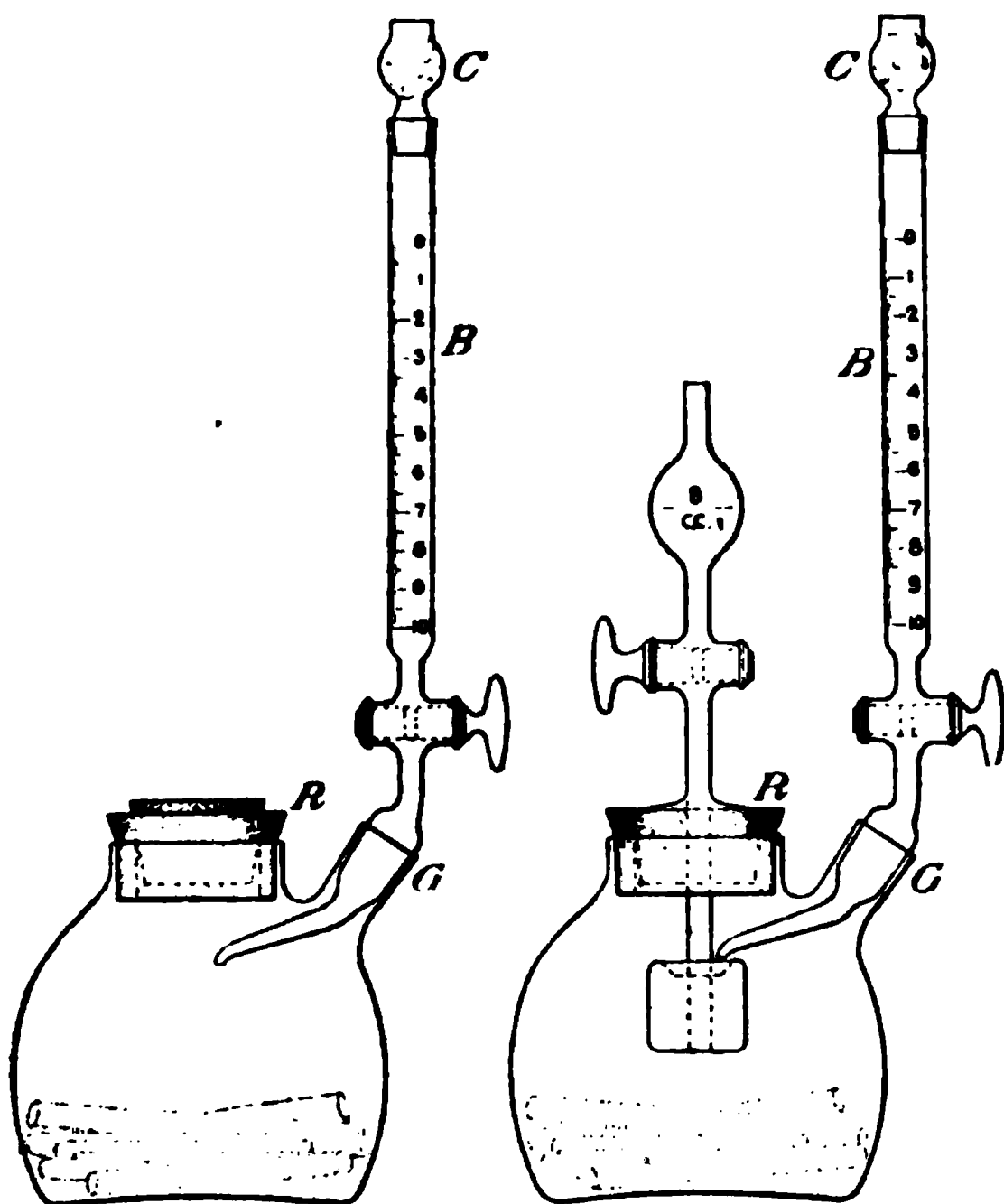


Fig. 2.

¹ Illustrations and descriptions of these apparatus are to be found in *Bull.* 238, Bureau of Plant Industry.

At 15-minute intervals the shaking is interrupted long enough to read the manometers. When the oxygen absorption has come to an end, as indicated by the identity of successive manometric readings, the experiment is considered completed.

If it is desired to determine approximately the carbon dioxide formed during the experiment, the ground joint *K* with the basket *H* is lifted off, a drop of phenolphthalein added and the basket *H* placed in the titration flask shown in Fig. 2. By rotating the buret *B* about the ground joint *G*, its tip is brought just above the basket. 0.1 *N* sulfuric acid is run into the basket during slow agitation until the appearance of the red color. The buret is then read; three drops of Congo red solution are placed in the basket and the titration continued until the bright red color disappears. From the difference between the two end points the amount of carbon dioxide absorbed may be calculated. In this fashion it is possible to carry out the titration in an atmosphere practically free from carbon dioxide, since the titration flask contains solid potassium hydroxide.

Experiments on the Effect of the Variable Factors Involved in the Method on the Total Oxygen Absorption.

In all of the experiments to be described in this publication the pressure readings on the manometer are given and these values reduced to the arbitrary volume of 150 cc. An absolute unit of oxidase content will be discussed at the end of the paper, but will not be made use of in the results given since the latter are only relative and have value only in proving the efficiency of the method. The juice used was freshly prepared for each experiment and, as it differed in each, different values were necessarily obtained from experiment to experiment.

TABLE I.—THE EFFECT OF VARYING THE CONCENTRATION OF PYROGALLOL.

Number of apparatus.	Volume of pyrogallol solution. cc.	Concentration of pyrogallol solution. Per cent.	Volume of potato juice. cc.	Content of glass basket.
1.....	8	10	2	1 cc. <i>N</i> NaOH
4.....	8	10	2	1 cc. <i>N</i> NaOH
5.....	8	5	2	1 cc. <i>N</i> NaOH
7.....	8	5	2	1 cc. <i>N</i> NaOH
11.....	8	2.5	2	1 cc. <i>N</i> NaOH
12.....	8	2.5	2	1 cc. <i>N</i> NaOH

11.20 A.M., put into thermostat; 11.45 A.M., began to shake. Rate of shaking—5 complete excursions, 3.1 seconds.

Table II shows that the absorption of oxygen comes to an end in the course of about 2 hours. In the following tables only this end result will be given. The full details have been included in the tables of the Bulletin.

TABLE II.

Time of reading of manometer.	Time elapsed since begin- ning of experi- ment expressed in minutes.	Temperature at the time of measurement expressed in degrees centigrade.	Manometer readings expressed in centimeters of mercury in apparatus.					
			No. 1.	No. 4.	No. 5.	No. 7.	No. 11.	No. 12.
11.45	0	36.4	0.00	0.00	0.00	0.00	0.00	0.00
12.00	15	36.4	0.50	0.60	0.52	0.55	0.70	0.65
12.15	30	36.4	0.62	0.80	0.90	0.80	1.00	1.05
12.30	45	36.4	0.85	0.95	0.98	0.80	1.20	1.10
1.30	105	36.4	1.25	1.40	1.32	1.60	1.70	1.30
1.45	120	36.4	1.40	1.60	1.40	1.60	2.20	1.40
2.00	135	36.5	1.50	1.58	1.45	1.65	3.20	1.50
2.15	150	36.4	1.58	1.80	1.60	1.80	Pyr. sol. splash into bulb.	1.60
2.30	165	36.5	1.70	1.80	1.70	1.80		1.60
Final readings corrected to a volume of								
150 cc. ¹			1.62	1.83	1.72	1.87		1.42

TABLE III.

Volume of pyrogallol solution used 8 cc.
Volume of potato juice used2 cc.
Content of glass basket.....1 cc. N NaOH.

Concentration of pyro- gallol solution used. Per cent.	Manometer readings expressed in centimeters of mercury in apparatus, corrected to a volume of 150 cc.
16.0	2.11
8.0.	2.48
4.0	2.64
2.0	2.60
1.0	2.86
0.5	2.76

In the following series fresh juice¹ was used, different from that in the experi-
ment just described.

0.80	1.39
0.40	1.46
0.20	1.22
0.10	0.31

The results shown in Tables I-III show definitely that the concentra-

¹ The apparatus used in all the experiments described in this paper (Fig. 1) have the approximate volume of 150 cc. They fluctuate in actual volume from 136 cc. to 156 cc. and all the corrections have to be made in order to make the volumes comparable. The apparatus of the latest form have the volume of 87 cc. and are all of the same size within 1 cc. This particular volume was chosen so that the actual volume of gas in the apparatus during the experiment would be 76 cc. and a change in pressure of 1 cm. of mercury under these conditions would correspond to the absorption of 1 cc. of oxygen. These apparatus may be obtained from Machlett & Son, 143 East 23d St., New York City.

tion of the pyrogallol solution has no appreciable effect on the end result, provided the concentration is above a certain lower limit, which in the experiments cited is a little more than 0.20%. It appears that a certain quantity of potato juice is capable of bringing about the oxidation of a very definite quantity of pyrogallol; quantities of pyrogallol present beyond this amount remain unoxidized. No attempt was made in the course of the work here described to determine exactly the smallest quantity of pyrogallol required; the experiments were carried out solely for the purpose of finding the concentration of pyrogallol solution necessary to obtain comparable results.

From Experiment 3 it is apparent that very great concentrations of pyrogallol, such as 16%, have a slight retarding action on the oxidation. This is especially noticeable in the rate with which the end point is reached.

On the strength of the results of these experiments it was decided to use, at least for the present, a 1% pyrogallol solution in all of the experiments to be made.

TABLE IV.—THE COMPARATIVE EFFECTIVENESS OF FRESH AND OF OLD PYROGALLOL SOLUTIONS.

Volume of pyrogallol solution used in each experiment		8.0 cc.
Volume of potato juice.....		2.0 cc.
Volume of N NaOH solution used in basket.....		1.0 cc.
Strength and age of pyro- gallol solution used.	Final pressure in apparatus ex- pressed in terms of cm. of mercury, corrected to a volume of 150 cc.	
1.0% old solution	1.82	
1.0% fresh solution	1.92	
0.1% old solution	0.79	
0.1% fresh solution	0.83	

This experiment was undertaken to determine whether it is necessary to prepare a fresh pyrogallol solution at the beginning of each experiment. As the experiment shows, the very old solution gives the same result as that freshly prepared and therefore no precautions need be taken in this respect. The difference between the results of the first pair and the second pair of the series is due to the low concentration of the pyrogallol in the latter (see Table III).

The fact that a definit quantity of juice is capable of bringing about the oxidation of a definit quantity of pyrogallol by a definit quantity of oxygen, led to the supposition that the total quantity of oxygen consumed in the oxidation of the pyrogallol in the presence of excess of the latter is directly proportional to the concentration of the oxidase in the juice. To test this hypothesis fresh potato juice was diluted with varying volumes of water and the activities compared. The results are given in Table V.

TABLE V.

Volume of 1 % pyrogallol solution 8.0 cc.		
Volume of N NaOH used in basket 1.0 cc.		
Amount of potato juice used. Cc.	Amount of water added to potato juice. Cc.	Manometer readings expressed in centimeters of mercury in apparatus.
2.0	0	1.73
2.0	0	1.89
1.0	1.0	0.97
0.5	1.5	0.38
0.5	1.5	0.48

This experiment shows that the total oxygen absorption is at least approximately proportional to the quantity of potato juice present. What the exact relationship is between the concentration of potato juice and the quantity of oxygen absorbed will be determined later.

Effect of Concentration of Alkali in the Absorption Basket on the Result.—It was necessary to determine the strength of the alkali solution required to insure prompt and complete absorption of the carbon dioxide produced during the experiments. For this purpose a number of experiments were carried out with varying concentrations of alkali in the basket, all other conditions being uniform.

TABLE VI.

Volume of 1 % pyrogallol solution. 8.0 cc.	
Volume of fresh potato juice 2.0 cc.	
Strength of NaOH used.	Manometer readings expressed in centimeters of mercury in apparatus.
2.50 N	2.10
1.00 N	1.73
0.50 N	2.08
0.25 N	1.98
0.10 N	1.73
0.00	0.80

As these results show, it is necessary to use at least 0.25 normal solution of sodium hydroxide to make sure of the complete removal of the carbon dioxide formed during the oxidation of the pyrogallol. To be certain of an excess of alkali, 1 cc. of a normal solution was used in all these experiments. There seems to be no doubt about the fact that under these conditions the absorption of the carbon dioxide from the atmosphere of the flasks is practically complete. This is borne out by the fact that in all of the experiments the reaction comes to completion within a few hours. If a measurable amount of carbon dioxide were unabsorbed in the oxidase apparatus, the pressure as indicated by the manometer would diminish as the shaking is continued until practically all of the carbon dioxide is absorbed.

Effect of the Rate of Shaking.—In the experiments cited, the oxidase apparatus were shaken at a rate of 5 complete excursions of the

machine in 3.0 seconds. Under these conditions in some cases a small amount of pyrogallol splashed into the alkali in the small glass basket (Table II). This became noticeable at once by an increased rate of oxygen absorption and the failure of the absorption to come to completion. It is impossible to overlook such an error for the following reasons: no experiment is taken into account unless the diminution of pressure comes to a definite end in the course of a few hours. To avoid accidents due to the splashing of pyrogallol into the basket the rate of shaking henceforth was reduced to 5 complete excursions in 3.3 seconds. Under these conditions, as will be seen, no difficulty due to splashing was ever experienced.

Effect of Temperature.—The temperature in the thermostat varied, as experiments given in Table VII shows, no more than 0.1° and it is certain that the maximal variations within the oxidase apparatus were less than that. Since the pressure is directly proportional to the absolute temperature, a rise of 0.1° at 36.4° will involve an increase of pressure of $\frac{76.0}{309.4 \times 10}$, i. e., 0.025 cm. of mercury. This is not greater than the errors involved in the measurements of the pressure existing within the oxidase apparatus.

TABLE VII.

Time of reading of manometer.	Time elapsed since beginning of experiment expressed in minutes.	Temperature at the time of measurement expressed in degrees centigrade.	Manometer readings expressed in centimeters of mercury in apparatus					
			No. 1.	No. 4.	No. 5.	No. 7.	No. 11.	No. 12.
10.00	0	36.4	0	0	0	0	0	0
			run in					
10.30	30	36.5	1.80	0	0	0	0	0
				run in				
11.00	60	36.4	2.10	1.25	0	0	0	0
					run in			
11.30	90	36.5	2.35	1.65	1.10	0		
						run in		
12.00	120	36.5	2.42	1.70	1.40	1.00	0	
							run in	
12.30	150	36.4	2.70	1.90	1.50	1.35	1.20	
								run in
1.00*	180	36.4	2.80	2.00	1.80	1.50	1.50	1.40
1.30	210	36.4	2.75	2.10	1.70	1.50	1.50	1.70
2.00	240	36.4	2.80	2.20	1.90	1.75	1.80	1.80
2.30	270	36.4	2.80	2.20	1.90	1.75	1.80	1.90

Final readings. Corrected to a volume of 150 cc..... 2.67 2.24 1.93 1.82 1.73 1.68

9.40 put into box; 10.00 began to shake. Rate of shaking—5 complete excursions, 3.4 seconds.

Effect of Shaking on the Activity of the Potato Juice.—Since it is known from the work of Meltzer, Schmidt-Nielssen and others that many of the enzymes lose their activity on vigorous shaking, it seemed advisable to see whether the potato juice loses its activity to any extent on account of the shaking during the experiments. This was hardly to be expected, since the rate of shaking employed was never very rapid.

To test the point in question three experiments were carried out as follows: Oxidase apparatus were clamped to the carriage of the shaking machine and the baskets charged with 1 cc. of normal sodium hydroxide. Into each apparatus were put 2 cc. of potato juice and 6 cc. of water. Two cc. of a 4% pyrogallol solution were placed in each of the graduated pipettes. In this fashion, after mixing, the usual dilutions were obtained. The pyrogallol solution was run into one apparatus just before the shaking was begun, into another some time later, into a third still later, and so on.

These results bring out a very remarkable fact. If the potato juice is shaken for 15–30 minutes before the addition of the oxidizable substance, its oxidizing power is reduced to about half its original value. On longer shaking no further effect is noticeable. Potato juice shaken for 2½ hours gives approximately the same result as that shaken only one hour. Whatever change the juice suffers takes place in the first hour of the experiment. The activity after this period is still quite appreciable and does not suffer any measurable loss on further shaking for 2–3 hours, which is the maximum duration of the measurements. This indicates that two phases of the process are dealt with, each one of which may be measured separately. In order to get the total oxidizing effect of the plant juice it is necessary to make the measurements right from the beginning when the shaking is begun.

These experiments very clearly point out the conditions under which the experiments must be carried out in order to obtain comparable results. The details of the method are based on these experiments and are described in an earlier part of this paper. The experiments also show that by means of this method it is possible to obtain quite accurate and reliable results, as shown by numerous parallel experiments carried out. It is true that in some of the duplicate experiments, especially in the beginning of the investigation, there are differences in the end results of from 2–3 mm. or even more (Experiments 11 and 12, Table II), but these differences become smaller as the work advances and the writer's experience with the apparatus grows.

It is intended to take up the results obtained and discuss their significance in a later paper on the mode of action of the oxidases in plant juices.

Practical Application of the Method to the Study of the Curly-Top Disease of Beets.

The Division of Cotton and Truck Diseases of the Bureau of Plant Industry, Department of Agriculture, has for some years been investigating the curly-top disease of sugar beets.¹ Through the courtesy of Mr. W. A. Orton and Mr. H. B. Shaw, the writer was able to obtain for experimental purposes fresh samples of sugar-beet leaves affected by this disease to a striking degree and also samples of normal beet leaves. All of the beets, of which the leaves were examined, were grown in a greenhouse, and therefore were subjected to practically uniform conditions. The leaves were treated in the same way as the potato peelings.

TABLE VIII.

Juice used.	Manometer readings expressed in centimeters of mercury in apparatus.	Grams of CO ₂ absorbed by alkali.
1. Juice of normal beet leaves.....	1.16	0.0015
2. Juice of normal beet leaves.....	1.07
3. Juice of diseased beet leaves.....	5.61	0.0050
4. Juice of diseased beet leaves.....	4.30	0.0040
5. Juice of normal beet leaves.....	1.10	0.0014
6. Juice of normal beet leaves.....	1.17	0.0016
7. Juice of diseased beet leaves.....	2.72	0.0031
8. Juice of normal beet leaves.....	1.19	0.0018
9. Juice of normal beet leaves.....	1.21	
10. Juice of diseased beet leaves (showing only slight symptoms).....	1.51	

Experiments given in Table VIII show a very striking difference between the juice of the normal and that of the diseased beet leaves. In all of the experiments the oxidase content as indicated by the oxygen absorption of the pyrogallol in the presence of the juice is markedly greater in the diseased than in the healthy leaves. The oxidase content of the normal leaves seems to be fairly constant, while the juice of the curly-top beet leaves shows wide variations. The leaves used in Experiment 3 give about 5 times as high a figure as normal leaves, while the leaves chosen in Experiment 10 show a variation of only 25% from the normal. It is very interesting to note that the deviation in oxidase content of the pathological leaves, as measured by the method described, runs parallel with the appearance of the leaves. The plants used in Experiment 3 showed very marked signs of curly-top, the leaves being small and shriveled, and the hairy roots abundant, while the diseased beet used in Experiment 10, which showed a relatively low oxidase content, but still higher than normal, had only a slight curling of the leaves.

It is fully realized that these experiments are subject to the criticism

¹ Shaw, Harry B., "The Curly-Top Disease of Beets," U. S. Dept. of Agr., Bureau of Plant Industry, *Bull.* 181, 1910.

that the juices of the two sets of leaves as prepared for the experiments may not be comparable. It may be merely an expression of the fact that one set of leaves is richer in cells than the other, or it might be that one is richer in water or in cellulose than the other. It is hoped to settle these questions in a future communication by paralleling the oxidase determinations with determinations of water, nitrogen, etc. Since the pathological leaves had in some cases more than three times the oxygen-absorbing power of the controls, it seems hardly possible, however, that this symptom can depend upon mere differences in the composition of the leaves.

Discussion of Results.

The main object of this paper is to describe a new method for the estimation of oxidases in plant juices. The method has been tested upon a number of samples of potato juice and found to give results in good agreement. There are still slight deviations between the results of duplicate determinations and efforts are being made at present to reduce these to a minimum. The main source of error lies in the rise of pressure within the oxidase apparatus, as soon as the shaking is begun.¹

A number of experiments have been carried out in which the influence of the variable factors of the method on the end result has been studied. Incidentally several very interesting facts came to light in the course of these experiments. The most important of these perhaps is the fact that only a very definite and limited quantity of oxygen is absorbed by pyrogallol in the presence of a definite quantity of potato juice within a short period of time, say 2 or 3 hours. Oxidation of the pyrogallol will proceed after that time but at a rate which is not measurable under the conditions of the experiment.

The concentration and total quantity of pyrogallol present is without effect on the end result, provided the pyrogallol is in excess. Within the limits of the experiments, the amount of the chemical change is directly proportional to the concentration of the oxidase present, all other factors remaining the same; doubling the volume of potato juice added doubles the volume of oxygen absorbed.

Chodat² working with *Lactarius* juice could not confirm the law of direct proportionality which he and Bach propounded for the action of peroxidase, but has experimental indications that the discrepancy is due to the inadequacy of his technique.

These facts are in contradiction to our conception of enzyme action in general. We are accustomed to look at enzymes as catalytic agents, quite analogous in their mode of action to the inorganic catalysts. If

¹ At present this difficulty is nearly entirely overcome by allowing the apparatus and the contents to stay at the temperature of experimentation for at least 30 minutes.

² "Mode de l'action de l'oxydase," *Arch. sci. phys. nat.*, 19, 501.

the substances in the potato juice which are responsible for the rapid absorption of oxygen by the pyrogallol were enzymes in the accepted sense of the word one would expect small quantities of the juice to bring about the oxidation of relatively large quantities of pyrogallol and that the oxidation would continue as long as pyrogallol and free oxygen are present, or until the activity of the juice is lost by deterioration. In the reaction discussed in this article, the process comes to completion when only a small definite portion of the pyrogallol is oxidized and while there is still an abundance of oxygen.

It seems therefore that the oxidase in potato juice accelerating the oxidation of pyrogallol by atmospheric oxygen is not an enzyme in the customary sense of the word, but rather a substance entering directly into the reaction and destroyed in the course of the same.

With the exception of a few isolated cases there exists no conception of what the composition of the so-called oxidases is; there are only theories as to their mode of action, and, on account of the diversity of the reactions they accelerate or bring about, as the case may be, we have not even a satisfactory definition to cover all of them. A starting point in their exact study must be made and it seemed to the writer necessary to take one type of reaction after another and correlate them, if possible, at the end. In this paper only the oxidation of pyrogallol by atmospheric oxygen has been considered and the method here worked out serves simply as a measure of the weight of oxygen that pyrogallol is capable of taking up in neutral aqueous solutions, due to the interaction of a certain volume of plant juice.

After the study of pyrogallol from this point of view has been exhausted, other compounds, such as hydroquinone, thymol, tannic acid, various sugars, etc., will be used. Then the reaction of the medium will be varied. It is hoped that on the basis of the experiments the oxidases may be classified.

Since it is desirable to express the strength of the juice in terms of some standard, the writer proposes as a unit for future experiments an oxidase solution of such strength that one liter of it will be capable of bringing about the consumption by pyrogallol of the equivalent of 1 gram of hydrogen, *i. e.*, of 8 grams of oxygen. This unit of "strength" may not have any relation to the rate of the absorption as it refers here explicitly only to the total amount absorbed. It is customary to let the "activity" of an enzyme be measured by the rate of action. It is an interesting question for future investigation whether the strength of an oxidase solution as expressed by this proposed standard is proportional to the rate at which the absorption takes place.

[CONTRIBUTION FROM THE PATHOLOGICAL DEPARTMENT OF ST. LUKE'S HOSPITAL,
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A NEW METHOD FOR THE DETERMINATION OF THE REDUCING SUGARS.

By E. C. KENDALL.

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In the study of velocity of amylolytic action it became desirable to determine with the greatest possible accuracy the reducing sugars resulting from the digestion of starch. This led to the following study of some modifications of Fehling's reagent with a view to establishing the optimum medium and conditions for a gravimetric method of determining reducing power.

Benedict¹ and others have pointed out the fact that glucose is more readily destroyed with sodium hydroxide than with sodium carbonate, and that larger amounts of copper are reduced by the same weight of sugar if sodium carbonate is used in place of sodium hydroxide. A comparison of the results obtained with three of the more common methods and a copper solution where the sodium hydroxide is replaced with sodium carbonate follows.

50 mg. of glucose reduces according to:

Defren's method.	Allihn's method.	Munsen and Walker's method.	Na ₂ CO ₃ solution replacing NaOH.
89.8 mg. Cu.	98.2 mg. Cu.	102.0 mg. Cu.	147 mg.

We thus see that the use of sodium hydroxide gives only about two-thirds of the amount of copper reduced which may be obtained with the carbonate.

After a series of experiments with the various alkalies, it was found that potassium carbonate was the one best suited to furnish the alkalinity. As the reducing power of glucose decreases with increase in the volume of the solution, it is necessary to have the volume of the solutions containing the copper and alkali which are added to the sugar solution as small as possible. Potassium carbonate is better than sodium carbonate, being much more soluble and having a slight advantage in giving more copper reduced for the same weight of glucose. Some experiments showing the relation between these two carbonates are as follows: 50 mg. of glucose gave with

- 5 g. sodium carbonate, 129.8 mg. copper.
- 10 g. sodium carbonate, 133.3 mg. copper.
- 15 g. sodium carbonate, 133.3 mg. copper.

All conditions being the same with

- 12 g. potassium carbonate, 140.4 mg. copper.
- 14 g. potassium carbonate, 142.8 mg. copper.
- 16 g. potassium carbonate, 140.4 mg. copper.

¹ *J. Biol. Chem.*, 3, 101 (1907); 5, 485 (1908).

Having found that potassium carbonate was best suited to furnish the alkalinity to the copper solution, it still remained to determine whether a better medium than Rochelle salts could be found to hold the copper in solution.

Some results according to Munson and Walker's method showed that unless the spontaneous reducing power of the alkaline tartrate solution is determined and allowed for, the results obtained will be considerably too high. Some results we obtained, using the method of Munson and Walker, but not allowing for the reducing power of the tartrate solution, are:

Sugar taken.	Copper found.	Sugar equivalent given in table.
60	126.5	62.4
60	124.6	61.4
100	203.0	102.5
100	202.7	102.3

In their original article¹ Munson and Walker give a series of figures showing the reducing power of their alkaline tartrate solution from day to day during the course of the investigation. These results varied from 0 to 2.0 mg. of cuprous oxide. Apparently the reducing power of the alkaline tartrate solution varies with different samples of Rochelle salts and it is imperative to make some correction for all samples which we have examined.

The amount of copper reduced by the alkaline tartrate seems to be much greater when the reduction takes place in a bath of boiling water than it does when the solution is heated for a short time over the flame as in Munson and Walker's method. By heating for 20 minutes in a bath of boiling water 50 cc. of the mixed Defren solution in a total volume of 150 cc. may reduce as much as 7 mg. of copper. Provided the reduction was caused by an impurity in the tartrate it would be possible to free the solutions from such impurities by treating the alkaline tartrate with a copper solution, reduce by heating in a bath of boiling water, filter, and use the resulting solution which would have no reducing power of its own. This was tried and it was then found that when such a solution was heated again in the boiling water a second reduction, as large as the first, took place. If the cuprous oxide was then filtered off and the solution again heated, a third reduction took place. Since this showed that the reduction is due to the tartrate itself, and that a previous reduction is not capable of removing the source of error, it seemed imperative to find some medium other than Rochelle salts for keeping the copper in solution.

Many compounds have been proposed for this purpose, among which

¹ THIS JOURNAL, 28, 663; 29, 541.

may be mentioned the bicarbonate solution of Soldaini¹ and the citrate solution proposed by Benedict.² In Benedict's volumetric method for the determination of sugar the disappearance of the blue color is taken as the end point of the titration and this method allows of an accurate determination of the sugar. Experiments were therefore made to see if Benedict's citrate solution could be adapted to a gravimetric method. It was then found that marked changes in the reducing powers of the sugars followed changes in concentration of the sodium carbonate and citrate.

Thus, using 50 mg. of glucose and 2 g. of copper sulfate in a volume of 150 cc., the following weights of copper, expressed in milligrams, were obtained under the conditions as given below, when heated for 20 minutes in a bath of boiling water:

Sodium citrate. Grams.	Sodium carbonate, 5 grams. Mg.	Sodium carbonate, 10 grams. Mg.	Sodium carbonate, 15 grams. Mg.
5	116.5	134.1	144.2
10	100.0	117.3	127.1
15	89.3	107.9	122.0
20	65.3	101.8	117.8

The change in the reducing power of sugar is explained only in part by assuming that the citrate solution dissolved the reduced cuprous oxide. This was shown by placing 150 mg. of Kahlbaum's cuprous oxide in each of four flasks and heating it under identical conditions of volume, time, and concentration of solution as in the above experiments. Oxidation of the cuprous oxide during the heating was prevented by displacing the air in the flask with illuminating gas and closing the flask with a two-hole stopper.

Determination of the copper content of 150 mg. of the cuprous oxide used showed on duplicate determination 125.6 and 126.1 mg. of copper, average 125.9 mg. All conditions being the same as above, the following weights of cuprous oxide were recovered after heating for 20 minutes:

Sodium citrate. Grams.	Sodium carbonate, 5 grams. Mg.	Sodium carbonate, 15 grams. Mg.
5	125.2	...
10	123.3	122.4
15	120.2	122.4
20	118.3	122.1

As 20 g. of sodium citrate in the presence of 5 g. of sodium carbonate could dissolve but 7.6 mg. of cuprous oxide the low results obtained with the sugar must be due to a depression of the reducing power of the sugar by the citrate. The results of other experiments in which the weights

¹ *Gas. chim. ital.*, 6, 322.

² *J. Biol. Chem.*, 5, 485 (1908).

of sugar varied showed that a citrate solution does not furnish a satisfactory solution in a gravimetric method.

As the spontaneous reduction of Rochelle salts and the depression and variations caused in the reducing power of sugar by sodium citrate are serious objections to these two salts, further work was done to find some other agent for holding the copper in solution.

Theoretically, any organic compound having a carboxyl and alcohol group is capable of holding the copper in solution in an alkaline mixture. Glycerol and mannite have also been suggested as possible agents, but they do not furnish a convenient solution with which to work. Lactic acid will hold the copper in solution, but the reducing power of sugar is but slight in such a solution.

Among a number of organic compounds which were tried, salicylic acid was found to be one which will furnish a medium for the reduction of sugar, but which has no reducing power of its own and will not dissolve the cuprous oxide.

An alkaline salicylate solution replacing the alkaline tartrate showed no reduction of copper when heated in a bath of boiling water for 7 hours, and the following results show that there is no appreciable change in reducing power with small changes in concentration of the salicylic acid.

50 mg. glucose. 5 grams sodium carbonate in 150 cc. volume.

3 grams salicylic acid, 125.7 mg. copper.

4 grams salicylic acid, 126.0 mg. copper.

5 grams salicylic acid, 125.7 mg. copper.

6 grams salicylic acid, 124.8 mg. copper.

Further experiments showed that with the other reducing sugars, maltose, lactose, and invert sugar, the alkaline salicylate solution furnishes a satisfactory medium for the reduction of the copper.

It now remained to determine what weights of copper, potassium carbonate and salicylic acid give the optimum conditions for the reduction of the copper.

In Munson and Walker's conditions 1.858 grams of copper sulfate (crystalline) are used per determination, the largest weight of copper reduced being 435.3 mg. While larger amounts of copper give greater reducing powers to the sugars, it was decided to use two grams of copper sulfate (crystalline) per determination and limit the reduction to 450 mg. of copper.

The weights of potassium carbonate and salicylic acid which give the optimum conditions for maltose were determined and these weights were used for the determination of the reducing power of the other sugars.

The effect of varying amounts of potassium carbonate and salicylic acid is shown in the following table. The volume was 140 cc. and 2 g. of copper sulfate were present:

Sugar maltose. Mg.	Salicylic acid. Grams.	Potassium carbonate,		
		12 g.	14 g.	15 g.
100	4	151.7	153.8	154.9
100	5	151.0	157.1	155.0
100	6	149.1	154.6	154.8
100	7	135.7	150.4	154.9

These and other determinations showed that 15 grams of potassium carbonate, 5 grams of salicylic acid, and two grams of copper sulfate in a total volume of 140 cc. give satisfactory conditions for the determination of maltose. The least volume of water which will conveniently dissolve the copper sulfate is 15 cc. and the least volume for the 15 grams of potassium carbonate is 25 cc. While it would be possible to make one solution of the three compounds, it was found that both copper and potassium salicylate are so slightly soluble that the volume of such a solution would be too great to give satisfactory results. The potassium carbonate and copper sulfate are therefore dissolved in water and added separately to the sugar solution while the salicylic acid is added in the dry condition.

In regard to the method of heating, the following experiments were carried out to determine whether or not any cuprous oxide was lost during the heating by surface oxidation:

150 mg. of Kahlbaum's cuprous oxide were placed in each of four flasks, 15 grams of potassium carbonate, 2 grams of copper sulfate and 5 grams of salicylic acid were added in a volume of 140 cc.

The weight of copper in 150 mg. of the cuprous oxide used was found to be 125.9 mg. The weights of copper recovered from the four flasks after the treatment indicated below were as follows:

1. Solution boiled over free flame under conditions of Munson and Walker, 124.5 mg. copper recovered.
2. Solution heated 20 minutes in bath of boiling water, 126.3 mg. copper recovered.
3. Solution heated 20 minutes in bath of boiling water with surface covered with toluene, 125.7 mg. copper recovered.
4. Solution heated 20 minutes in bath of boiling water, air above solution being displaced with illuminating gas, 126.3 mg. copper recovered.

These results showed that there is no appreciable loss of cuprous oxide due to surface oxidation when the heating is continued for 20 minutes in the boiling water.

The two methods of heating which have been used for the reduction of copper with sugar are by heating over a free flame or in a bath of boiling water. In choosing between these two methods, ease of operation, time required, and accuracy of the results obtained were the factors considered.

The following results bear on this point:

The conditions of the solutions in each of the following sets were those found to be the optimum conditions for determining the reducing power of sugars. Volume 140 cc., potassium carbonate 15 grams, salicylic acid 5 grams, copper sulfate 2 grams.

HEATING IN BATH OF BOILING WATER.

Time. Min.	Glucose, 50 mg. Mg. Cu.	Invert sugar, 50 mg. Mg. Cu.	Lactose, 100 mg. Mg. Cu.	Maltose, 100 mg. Mg. Cu.
10	132.7	142.4	123.6	124.8
15	145.1	152.5	144.5	144.8
20	149.8	154.7	154.4	153.1
25	150.1	157.4	161.1	158.5
30	155.0	162.9	165.4	163.3
40	157.1	164.9	171.6	167.9
50	159.9	166.3	176.2	172.2

HEATING OVER FLAME.

Total time of heating. Min.	Time of boiling. Min.	Glucose, 50 mg. Mg. Cu.	Lactose, 100 mg. Mg. Cu.
6	2	112.2	103.0
8	4	134.1	132.8
9	5	137.1	139.0
12	8	143.8	154.1
14	10	143.0	161.1
16	12	148.3	163.6
18	14	150.4	167.3
20	16	153.4	169.4

The figures in the first line of the last table above give the weights of copper reduced under the conditions of Munson and Walker. It is apparent that the reduction under these conditions is far from complete and that the speed of reaction at this point is too great to allow of an accurate determination of reducing power. The reason for the incomplete reduction after two minutes' boiling is undoubtedly due to the slower reaction of the carbonate-salicylate solution than of the hydroxide-tartrate solution.

When the determinations of reducing power are done in sets of four or more time is saved per determination by making the time of heating as short as possible. However, it is evident that at least twelve minutes of boiling over a flame are required. When the time of heating is limited to twelve minutes it is impossible to filter one set while the following set is being heated, but if the time of heating be extended it is possible to give one's entire attention to filtering the reduced copper and hence there is no actual loss of time per determination.

To boil a solution over a flame for twelve to sixteen minutes requires more or less attention to maintain uniform conditions, but it is an easy

matter to duplicate conditions of heating in a bath of boiling water and no attention is required during the heating. Furthermore, it was found that the results obtained by heating in boiling water are more accurate than those obtained by boiling the solution. After twenty minutes' heating in boiling water the reaction is nearly complete for glucose and invert sugar and there is only a slow rate of reduction for lactose and maltose. As heating beyond 20 minutes would mean a needless expenditure of time, it was decided to limit the reduction for all of the sugars to that obtained during 20 minutes' heating in boiling water.

Although the salicylic acid is employed in the alkaline solution and must, therefore, exist as potassium salicylate, it was found impossible to replace the acid with sodium salicylate and obtain the same reducing power for maltose.

The following results show the difference between the free acid and the sodium salt:

Grams.	Sodium salicylate.	Salicylic acid.
3	117.4	141.3
4	126.0	143.1
5	131.9	148.4
6	136.2	148.7

The volume was 125 cc., 2 g. copper sulfate, 11.5 g. potassium carbonate, and 100 mg. of maltose being present. The figures are milligrams of copper reduced.

When the salicylic acid and sodium salicylate were kept constant and the potassium carbonate varied, the following results were obtained:

Potassium carbonate. Grams.	Sodium salicylate, 3 grams. Mg. Cu.	Salicylic acid, 3 grams. Mg. Cu.
15	123.1	145.6
18	125.7	146.8
21	130.4	148.1
24	135.8	151.9

The volume was 125 cc., 2 g. of copper sulfate and 100 mg. maltose were used.

Another series where more salicylic acid and sodium salicylate were used gave the following results:

Potassium carbonate. Grams.	Sodium salicylate. Grams.	Copper.
15	6	138.3
18	6	142.1
21	6	144.3
24	6	147.8
Potassium carbonate. Grams.	Salicylic acid. Grams.	Copper.
12	6	148.1
15	6	152.6
18	6	157.0
21	6	158.3

Although it would seem to make no difference when the sugar was added to the solution of potassium-copper salicylate, experiment showed that it is necessary to add the copper to the solution and not *vice versa*. A series where 15 g. of potassium carbonate and 5 g. of salicylic acid were used and 100 mg. of maltose were added to this solution gave 152.6, 146.2, 149.1, and 156.2 mg. of copper reduced. Under identical conditions, but where the copper solution was added to the sugar, the following weights of copper were obtained: 154.9, 155.0, 154.8, 154.9.

The effect of mixing the sugar and alkaline copper solutions and allowing to stand in the cold is shown by the following results: To four flasks, each containing 100 cc. of water, 100 mg. of lactose and 25 cc. of copper sulfate (2 grams) were added. At intervals of five minutes, 12 grams of potassium carbonate and 3 grams of salicylic acid were added to the four flasks in succession. The flask to which the potassium carbonate and salicylic acid was first added would have stood 15 minutes before the mixture had been added to the fourth flask. As soon as the fourth flask was ready they were all placed in the boiling water and allowed to remain 20 minutes; the following weights of copper were obtained:

Solution stood in the cold 15 min., 149.8.

Solution stood in the cold 10 min., 147.4.

Solution stood in the cold 5 min., 146.3.

Solution stood in the cold 0 min., 146.5.

These results show that the sugar can stand in the alkaline copper solution for 5–6 minutes in the cold without any appreciable change, but that a slight reduction will occur if they are allowed to stand 10–15 minutes. In practice 2–3 minutes is all that is needed to dissolve the salicylic acid and prepare the solutions for the boiling water.

The temperature at which the solutions are added to the boiling water is without appreciable influence between 18° and 50°. Four solutions, each containing 12 g. potassium carbonate, 3 g. salicylic acid, 2 g. copper sulfate, and 100 mg. lactose, when placed in the boiling water at the indicated temperature gave the following weights of copper reduced:

18°, 150.4 mg. copper; 30°, 150.7 mg. copper; 40°, 150.7 mg. copper; 50°, 151.5 mg. copper.

It is essential to have the boiling water heated with a flame large enough to cause the water to begin boiling within 1.5–2 minutes after the addition of the flasks containing the sugar-copper solutions.

Two flasks, containing 12 g. of potassium carbonate, 3 g. of salicylic acid, 2 g. of copper sulfate, and 120 mg. of lactose in 125 cc., were placed in the boiling water with a flame under the bath, which caused the water to boil within 1.5–2 minutes after the flasks were placed in the bath. The copper reduced at the end of 20 minutes was 175.5 and 176.3 mg.

Two other flasks containing identical solutions were placed in the boiling water with a flame under the bath which caused the water to boil in 5-6 minutes after the addition of the flasks. After 20 minutes from the time the flasks were placed in the water the copper reduced was 167.9 and 171.8 mg., showing lower and irregular results.

In order to show the variations caused by slight differences in the weights of potassium carbonate and salicylic acid added, the following series of determinations were made under identical conditions of time and volume. The volume was 140 cc. and time 20 minutes:

Potassium carbonate. Grams.	Salicylic acid. Grams.	Glucose, 50 mg.	Invert sugar, 50 mg.	Lactose, 100 mg.	Maltose, 100 mg.
15	4	148.9	155.2	160.0	154.9
15	5	149.2	155.7	157.2	155.0
15	6	...	156.7	154.9	154.9
15	7	150.0	158.0	151.4	154.9
13	5	151.4	...	152.9	153.0
14	5	151.4	158.3	154.5	154.6
15	5	149.4	155.7	157.2	155.0
16	5	149.4	156.1	156.9	156.3
17	5	147.3	155.5	160.1	158.4

These results show that glucose, maltose, and invert sugar vary but slightly for differences in amounts of potassium carbonate and salicylic acid present and that lactose is more sensitive in this respect.

In practical determinations of sugar, the variations in the weights of potassium carbonate and salicylic acid can be controlled within ± 0.2 g. without taking any special precautions and it is apparent that such a variation causes no appreciable change in the reducing power of any of the sugars.

Determination of the Copper Reduced.

In a recent number of *THIS JOURNAL* the writer described a method for the determination of copper by means of the iodide method. The method, as there described, was devised primarily for the determination of copper obtained by the reduction with sugar. It differs from the original iodide method in that the solutions are prepared for titration in the cold, thus overcoming the delay caused by boiling the solution or evaporating to dryness.

During the course of this investigation several hundred determinations of copper have been made by this modification of the iodide method, and these results show that, if the conditions prescribed are followed, the determination of copper can be made by this method with great accuracy. Irrespective of the way the reduced copper is determined it has to be removed from its filter, and the most convenient way to do this is to dissolve it in nitric acid. The iodide method allows of the accurate

determination of the copper *thus dissolved*, hence doing away with drying and weighing, which is time-consuming and laborious.

The cuprous oxide reduced by the sugar is filtered on a glass funnel such as is usually employed to hold a Gooch crucible. The filter is made by placing a perforated porcelain disk in the bottom of the funnel and making an asbestos felt 6 to 8 mm. in thickness. A porcelain disk should be used to hold the asbestos, as glass wool retains traces of the alkaline copper solution. After the solution has been filtered with suction and washed with hot water, the funnel and rubber stopper are removed from the suction flask, washed free from any copper solution which may adhere to the outside, and placed on a 350 cc. suction flask. If the stopper does not fit, the top of the flask is ground smooth on a carborundum hone so that when suction is applied it will hold the stopper down tightly over the mouth. Before the suction is applied to the flask the cuprous oxide is dissolved in not less than 10 cc. of *hot* nitric acid (1 part of acid to 3 of water). It is imperative to have the nitric acid hot and it should be contained in a wash bottle which delivers a small stream. The flask in which the reduction takes place and the sides of the funnel are washed with the hot acid and then the asbestos is stirred up by the jet from the wash bottle. It is best not to have a porcelain disk on the surface of the asbestos. The hot nitric acid will dissolve only a trace of nitrous oxide, but if cold nitric acid is used large amounts of nitrous acid will be dissolved, which will prevent the accurate determination of the copper. When all of the cuprous oxide has been dissolved the suction is applied and the funnel is washed with several additions of small amounts of water—not more than 10–12 cc. at a time. The wash water is sucked through each time before more is added. All of the copper, when washed in this way, can be removed with 40–50 cc. of wash water. The copper in solution may now be determined as described in the method.¹

Preparation and Analysis of the Sugars Used.

The four sugars used to determine the relation between sugar and copper given in the table below were prepared and analyzed as follows:

The glucose of highest purity, furnished by Merck & Co., when analyzed for moisture and rotating power showed 0.16% of moisture and a specific rotating power of 52.68°. As the specific rotating power was in accordance with that given by Tollens for pure glucose no further purification was considered necessary.

The sucrose was prepared from Kahlbaum's C. P. saccharose by the method outlined by the International Commission for the Unification of Sugar Analysis. The sample thus prepared contained 0.13 per cent. of moisture and showed a specific rotating power of 66.5°.²

¹ THIS JOURNAL, 33, 1947.

² The sucrose was inverted essentially by the method used by Munson and Walker

The lactose was prepared from Kahlbaum's crystallized lactose by dissolving in boiling water, filtering, and allowing the lactose to crystallize for seven days from this solution. These crystals were dried in a vacuum over sulfuric acid for three days, ground into a powder, and again dried in vacuum over sulfuric acid. The determination of moisture showed 5.62% of water. One molecule of water, corresponding to the formula $C_{12}H_{22}O_{11} \cdot H_2O$, requires 5.0% of water, therefore the sample thus prepared contained 0.62% excess water calculated as lactose hydrate. Its specific rotating power calculated as $C_{12}H_{22}O_{11} \cdot H_2O$ was 52.51° .

The maltose was prepared by letting barley diastase act on soluble starch as described by Baker and Day¹ and Baker.² The maltose thus prepared was dried in an electric oven at $70-80^\circ$ for 15-18 hours, and was then ground and passed through a 60-mesh sieve. The moisture determination showed 5.33% of water. As maltose hydrate, $C_{12}H_{22}O_{11} \cdot H_2O$, requires 5% of water there was present 0.33% excess water. The specific rotating power was 137.3° .

The rotating power of all preparations was determined with sodium light, using a 4 decimeter tube in a Schmidt and Haensch polariscope at 20° . The solutions were 10% of sugar, except for maltose, which was 5%. The solutions, except for sucrose, were allowed to stand 24 hours at room temperature to destroy the multirotation.

The water content of all preparations were determined as follows: Two grams of the sample in a small weighing bottle was placed in the bottom of a 4-inch desiccator which had a suction outlet in the lid. Around the weighing bottle was placed a wire gauze collar about 1.75 inches in diameter. This wire gauze supported a Petri dish of 3 inches diameter which contained phosphorus pentoxide. A second Petri dish of almost the same diameter as the desiccator was supported above the first Petri dish by three wire supports at a distance of 0.5 inch above the lower Petri dish. This top Petri dish acted as a cover and prevented the phosphorus pentoxide from dusting when the suction was released. After placing the cover on the desiccator it was placed inside an electric oven and connected with stout suction hose to a Gaede pump. The temperature of the oven was kept for lactose at 130° , maltose 110° , sucrose and glucose 100° , for 4-5 hours. The suction was maintained during the entire time of heating. At intervals of one hour the weighing bottle was taken out of the desiccator and weighed. When heating for one hour produced a change of less than 0.5 mg. the heating was discontinued. Duplicate determinations were made in all cases.

by heating for 30 minutes in boiling water with $N/10$ HCl, using 20 cc. for every 100 cc. final volume. The solution was barely neutralized with $N/10$ sodium hydroxide, cooled and filled at 20° to the mark of graduation.

¹ *Analyst*, 33, 393 (1908).

² *J. Chem. Soc.*, 1902, 1177.

Determination of Relation between Sugar and Copper.

For maltose and lactose the sugar was weighed out in such quantities as to make 5 mg. per cc. of solution, allowance being made for the presence of the water; the weights of sugar were calculated as maltose and lactose hydrate, $C_{12}H_{22}O_{11} \cdot H_2O$.

For invert sugar and glucose, solutions were made which contained 2.5 mg. of sugar calculated as $C_6H_{12}O_6$.

The temperature of graduation of both flasks and burets was 20°.

The Reducing Power of the Sugars

was determined as follows: The varying weights of sugar as indicated below were measured into 200 cc. Erlenmeyer flasks and the volume in each case made up to 100 cc. with distilled water. 5 grams of salicylic acid were now added to each of four flasks containing the sugar to be determined. Fifteen cc.¹ of copper sulfate solution and then 25 cc. potassium carbonate² solution were added to each of the flasks without any agitation of the solution. It was found necessary to observe this order for the addition of the reagents. The flasks were then shaken with a rotary motion. The precipitate of copper carbonate dissolved, forming a dark green solution. As soon as the salicylic acid dissolved the four flasks were put in a holder and placed in a bath of boiling water.³ The

¹ The copper sulfate solution is prepared by dissolving 133.33 grams of $CuSO_4 \cdot 5H_2O$ per liter of water; 15 cc. of such a solution contains 2 grams of copper sulfate.

² The potassium carbonate solution contains 600 g. of anhydrous potassium carbonate per liter. 25 cc. of this solution contains 15 g. of potassium carbonate. As potassium carbonate is hygroscopic it is necessary to drive off all water before making up the solution. This is done by heating the carbonate for 3-4 hours at a temperature from 190° to 200°. A sample of the salt thus treated when heated in a small test tube should not give any evidence of liberation of water. The carbonate solution should be made up in a liter or other size graduated flask and should be diluted almost to the proper volume well mixed, and then adjusted to the mark of graduation.

³ The water bath used during this investigation was one 10 inches in diameter and 6½ inches deep. It contained 4 liters of water. The level of the water could be maintained constant by using the ordinary constant water level bath, or by means of a syphon acting between the water bath and a reservoir of water of constant level. The syphon for constant use must have a T or Y tube inserted at its highest point. A 20 cc. pipet closed at one end with rubber hose and pinchcock is connected with the T-tube. To start the syphon both ends are placed under water and (the pinchcock being open) the air is withdrawn from the pipet. When the pipet is full of water the pinchcock is closed. Any bubbles of air liberated from the water in the tube of the syphon will rise to the highest point of the tube and will there be caught in the pipet, displacing the water. Should the pipet become filled with air the syphon may be re-established by again withdrawing the air through the rubber tube and pinchcock. The end of the syphon which is in the water bath must have a small opening (about 1/8 in.). If a large opening is used the water when boiling may syphon out of the bath. The diameter of the rest of the syphon may be of any sized tubing.

The flame under the water bath was supplied by one large-sized Fletcher and two Bunsen burners. The water should be boiling vigorously when the flasks are placed

flame under the bath must be of such size that boiling begins within 1.5–2 minutes after addition of the flasks. At the end of twenty minutes from the time the flasks were placed in the bath the solutions were filtered and the copper determined as described above.

TABLE I.

Weight of sugar. Mg.	Glucose.		Invert sugar.		Weight of sugar. Mg.	Lactose.		Maltose.	
10	30.4	30.2	30.9	30.7	20	31.9	32.1	31.0	30.3
20	60.9	61.8	63.2	62.4	40	64.0	62.5	61.0	61.3
30	90.2	90.6	94.4	94.7	60	95.5	95.2	93.4	92.3
40	120.0	120.1	126.5	126.8	80	124.5	125.0	123.6	123.6
50	148.1	149.9	157.5	156.7	100	157.7	157.7	154.6	154.6
60	176.8	179.2	188.2	186.4	120	287.4	286.3	187.9	187.2
70	206.1	207.4	{ 217.5 219.7 }	{ 217.5 215.6 }	140	218.5	217.0	219.2	218.5
80	233.8	233.8			160	246.3	246.7	250.6	250.4
90	261.3	263.3	276.1	276.1	180	279.0	278.4	278.6	280.1
100	288.0	289.2	302.6	302.6	200	306.8	305.9	{ 309.6 *313.6 310.9 *312.4 }	{ 309.6 *313.6 310.9 *312.4 }
110	316.2	314.7	330.8	330.7	220	338.7	337.1	342.2	342.2
120	343.1	341.5	359.4	358.6	240	{ 364.6 364.9 }	*363.4	373.3	372.9
130	367.7	367.7	385.5	386.4	260			403.2	401.6
140	391.2	393.0	410.9	410.9	280	424.9	427.0	{ 431.4 431.4 }	{ 431.4 *429.4 }
150	418.5	418.5	438.1	438.1	300	455.6	454.3		
160	443.3	442.1	462.1	460.9

in the water and all of the flames should be burning. As soon as the water has begun to boil after the addition of the flasks (which should be in less than two minutes) the two bunsen burners are turned out as the Fletcher burner is sufficient to maintain the boiling.

In the practical application of this method for the determination of the reducing sugars, it is most convenient to make a set of 4 determinations at once. A rack is made to hold the 4 flasks as follows: a brass rod 1/4 inch in diameter and 14 inches long is erected at the center point and perpendicular to a brass disk 8 inches in diameter and 1/8 inches thick. This disk forms the bottom upon which the flasks are placed. Another disk of the same size as the bottom one, but with a hole 3/16 inch in diameter, slides up and down the rod. Four holes 1 1/2 inches in diameter are drilled through this second disk, the centers of the holes being arranged symmetrically 2 1/4 inches from the center of the disk. This top disk being lifted up the four flasks are placed on the bottom of the holder. When the top disk is lowered the flasks will pass through the four holes, and as the opening is only sufficiently large to allow the neck of the flask to pass through, the flasks are held secure. A hook at the end of the rod is used to hang the entire holder from a support above the bath at such a height that the rack sinks in the water up to the level of the top disk. In the bottom disk a number of 1/8-inch holes are drilled so that the rack may be placed in and removed from the water with ease. When the flasks are removed from the rack the solutions are filtered immediately on four suction flasks.

TABLE II.

Glucose.			Invert sugar.			Lactose.			Maltose.		
Found. Mg.	Calculated. Mg.	Error. Mg.	Found. Mg.	Calculated. Mg.	Error. Mg.	Found. Mg.	Calculated. Mg.	Error. Mg.	Found. Mg.	Calculated. Mg.	Error. Mg.
30.3	30.6	0.3	30.8	31.43	0.63	32.0	32.07	0.07	30.6	30.2	-0.40
61.4	60.9	-0.5	62.8	63.55	0.75	63.3	63.38	0.08	61.2	61.96	0.76
90.4	90.8	0.4	94.6	95.24	0.64	95.4	94.52	-0.88	92.9	93.57	0.67
120.1	120.3	0.2	126.7	126.44	-0.26	124.8	125.48	0.68	123.6	125.02	1.42
149.0	149.4	0.4	157.1	157.15	0.05	157.7	156.28	-1.42	154.6	156.32	1.72
178.0	178.1	0.1	187.3	187.37	0.07	186.9	186.90	0	187.6	187.47	-0.13
206.8	206.4	-0.4	217.7	217.10	-0.60	217.8	217.34	-0.46	218.9	218.47	-0.43
233.8	234.3	0.5	245.5	246.33	0.83	246.5	247.60	1.10	250.5	249.32	-1.18
262.3	261.7	-0.6	276.1	275.07	-1.03	278.7	277.70	-1.00	279.4	280.04	0.64
288.6	288.8	0.2	302.6	303.33	0.73	306.4	307.63	1.23	310.1	310.59	0.29
315.5	315.5	0	330.8	331.09	0.29	337.9	337.38	-0.52	342.2	341.00	-1.20
342.3	341.7	-0.6	359.0	358.35	-0.65	364.8	366.95	2.15	373.1	371.25	-1.85
367.7	367.6	-0.1	386.0	385.14	-0.86	397.2	396.35	-0.85	402.4	401.35	-1.05
392.1	393.0	0.9	410.9	411.43	0.53	426.0	425.58	-0.42	431.4	431.31	-0.09
418.5	418.1	-0.4	438.1	437.23	-0.87	455.0	454.64	-0.36	458.7	461.12	2.42
442.7	442.7	0	461.5	462.55	1.05

TABLE III.

Method.	Dextrose.		Invert sugar.		Lactose.		Maltose.	
	50 mg.	100 mg.	50 mg.	100 mg.	100 mg.	200 mg.	100 mg.	200 mg.
Defren.....	89.8	178.1	125.7	248.4	109.5	216.5
Munson and Walker.....	102.2	198.4	98.5	192.3	132.7	261.6	108.7	215.4
Allihn.....	98.2	195.0
Lehmann.....	101.4	190.0
Meissl.....	96.0	189.2
Soxhlet.....	138.3	269.6
Wein.....	115.1	226.8
Ost.....	165.6	294.3	170.0	298.0	167.5	331.8
Kjeldahl.....	107.2	197.7	101.7	190.2
Brown, Morris and Millar.....	103.0	202.7	97.5	194.1
This method...	149.3	288.7	157.0	303.3	156.3	307.6	156.3	310.6

Using this method of procedure the results in Table I were obtained for the indicated weights of sugar. All of the results which were obtained are given, but the ones which were not used in the calculation of the curve are starred:

From these results the following equations showing the relation between sugar and copper were deduced by means of the method of least squares.¹

In the equations X refers to weights of copper reduced, Y to weights of sugar reacting:

Glucose..... $X = -0.17 + 3.0923 Y - 0.002026 Y^2$

Invert sugar..... $X = -1.30 + 3.2918 Y - 0.002455 Y^2$

Lactose..... $X = 0.59 + 1.5786 Y - 0.000217 Y^2$

Maltose..... $X = -1.69 + 1.5988 Y - 0.000187 Y^2$

The weights of sugar given in Table IV were substituted in the proper equation and the corresponding values of X were found. The differences between the values thus calculated and actually found is given in Table II.

By means of the equation the copper equivalent to weights of maltose and lactose from 20 to 300 mg. were calculated for every 4 mg. of sugar. With glucose and invert sugar the copper equivalent for every two mg. of sugar from 10 to 160 was found. This gave a series of points which differed by about six mg. of copper. These figures were changed to integral weights of copper and hence decimal weights of sugar. The figures lying between each six mg. of copper were interpolated, the interpolations being carried to the second decimal place. The complete table giving the relation between the four reducing sugars and copper for every mg. of copper from 30 to 450 mg. is given in Table IV.

A comparison of the reducing power of the sugars obtained by this method with that obtained with other methods in use is given in Table III.

TABLE IV.

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11}.H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11}.H_2O$.
30	33.8	37.6	9.8	9.6	19.3	19.9
31	34.9	38.8	10.2	9.9	20.0	20.5
32	36.0	40.1	10.5	10.2	20.6	21.1
33	37.2	41.3	10.8	10.5	21.2	21.7
34	38.3	42.6	11.1	10.8	21.8	22.4
35	39.4	43.8	11.5	11.1	22.5	23.0
36	40.5	45.1	11.8	11.4	23.1	23.6
37	41.7	46.3	12.1	11.8	23.7	24.3
38	42.8	47.6	12.4	12.1	24.4	24.9
39	43.9	48.8	12.8	12.4	25.0	25.5
40	45.0	50.1	13.1	12.7	25.6	26.1

¹ A good example of the use of this method is given in Allihn's original article, *J. prakt. Chem.*, 22, 46 (1880).

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
41	46.2	51.3	13.4	13.0	26.3	26.8
42	47.3	52.6	13.8	13.3	26.9	27.4
43	48.4	53.8	14.1	13.6	27.5	28.0
44	49.5	55.1	14.4	13.9	28.1	28.7
45	50.7	56.3	14.8	14.2	28.8	29.3
46	51.8	57.6	15.1	14.5	29.4	29.9
47	52.9	58.8	15.4	14.8	30.0	30.6
48	54.0	60.1	15.7	15.2	30.6	31.2
49	55.2	61.3	16.1	15.5	31.3	31.8
50	56.3	62.6	16.4	15.8	31.9	32.4
51	57.4	63.8	16.7	16.1	32.5	33.1
52	58.5	65.1	17.1	16.4	33.2	33.7
53	59.7	66.3	17.4	16.7	33.8	34.3
54	60.8	67.6	17.7	17.0	34.4	35.0
55	61.9	68.8	18.1	17.3	35.0	35.6
56	63.0	70.1	18.4	17.6	35.7	36.2
57	64.2	71.3	18.7	17.9	36.3	36.9
58	65.3	72.6	19.1	18.3	36.9	37.5
59	66.4	73.9	19.4	18.6	37.6	38.1
60	67.6	75.1	19.7	18.9	38.2	38.8
61	68.7	76.4	20.0	19.2	38.8	39.4
62	69.8	77.6	20.4	19.5	39.4	40.0
63	70.9	78.9	20.7	19.8	40.1	40.7
64	72.1	80.1	21.0	20.1	40.7	41.3
65	73.2	81.4	21.4	20.5	41.3	41.9
66	74.3	82.6	21.7	20.8	41.9	42.5
67	75.4	83.9	22.0	21.1	42.6	43.2
68	76.6	85.1	22.4	21.4	43.2	43.8
69	77.7	86.4	22.7	21.7	43.8	44.4
70	78.8	87.6	23.0	22.0	44.4	45.1
71	79.9	88.9	23.4	22.3	45.1	45.7
72	81.1	90.1	23.7	22.7	45.7	46.3
73	82.2	91.4	24.0	23.0	46.3	47.0
74	83.3	92.6	24.4	23.3	46.9	47.6
75	84.4	93.9	24.7	23.6	47.5	48.2
76	85.6	95.1	25.0	23.9	48.1	48.9
77	86.7	96.4	25.4	24.2	48.8	49.5
78	87.8	97.6	25.7	24.5	49.4	50.1
79	88.9	98.9	26.0	24.9	50.0	50.8
80	90.1	100.1	26.4	25.2	50.7	51.4
81	91.2	101.4	26.7	25.5	51.3	52.0
82	92.3	102.6	27.1	25.8	51.9	52.7
83	93.4	103.9	27.4	26.1	52.6	53.3
84	94.6	105.1	27.7	26.4	53.2	53.9
85	95.7	106.4	28.1	26.8	53.9	54.6
86	96.8	107.6	28.4	27.1	54.5	55.2
87	97.9	108.9	28.7	27.4	55.1	55.8
88	99.1	110.1	29.1	27.7	55.8	56.5

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
89	100.2	111.4	29.4	28.0	56.4	57.1
90	101.3	112.7	29.7	28.3	57.1	57.7
91	102.4	113.9	30.1	28.7	57.7	58.3
92	103.6	115.2	30.4	29.0	58.4	58.9
93	104.7	116.4	30.8	29.3	59.0	59.6
94	105.8	117.7	31.1	29.6	59.7	60.2
95	106.9	118.9	31.4	29.9	60.3	60.9
96	108.1	120.2	31.8	30.2	60.9	61.5
97	109.2	121.4	32.1	30.6	61.6	62.2
98	110.3	122.7	32.4	30.9	62.2	62.8
99	111.5	123.9	32.8	31.2	62.8	63.4
100	112.6	125.2	33.1	31.5	63.5	64.1
101	113.7	126.4	33.5	31.8	64.2	64.7
102	114.8	127.7	33.8	32.2	64.8	65.3
103	116.0	128.9	34.1	32.5	65.4	66.0
104	117.1	130.2	34.5	32.8	66.1	66.6
105	118.2	131.5	34.8	33.1	66.8	67.2
106	119.3	132.7	35.2	33.4	67.4	67.8
107	120.5	134.0	35.5	33.8	68.0	68.5
108	121.6	135.2	35.9	34.1	68.7	69.1
109	122.7	136.5	36.2	34.4	69.3	69.8
110	123.8	137.7	36.6	34.7	70.0	70.4
111	125.0	139.0	36.9	35.0	70.6	71.1
112	126.1	140.2	37.2	35.4	71.3	71.7
113	127.2	141.5	37.5	35.7	71.9	72.3
114	128.3	142.7	37.9	36.0	72.6	73.0
115	129.4	144.0	38.2	36.3	73.2	73.6
116	130.6	145.2	38.5	36.7	73.8	74.2
117	131.7	146.5	38.9	37.0	74.5	74.9
118	132.8	147.7	39.2	37.3	75.1	75.5
119	134.0	149.0	39.6	37.6	75.8	76.2
120	135.1	150.2	39.9	37.9	76.4	76.8
121	136.2	151.5	40.3	38.3	77.1	77.4
122	137.4	152.7	40.6	38.6	77.7	78.1
123	138.5	154.0	40.9	38.9	78.4	78.7
124	139.6	155.2	41.3	39.2	79.0	79.4
125	140.7	156.5	41.6	39.5	79.7	80.0
126	141.9	157.7	42.0	39.9	80.3	80.6
127	143.0	159.0	42.3	40.2	81.0	81.3
128	144.1	160.2	42.6	40.5	81.6	81.9
129	145.2	161.5	43.0	40.8	82.3	82.5
130	146.4	162.7	43.3	41.2	82.9	83.2
131	147.5	164.0	43.7	41.5	83.6	83.8
132	148.6	165.2	44.0	41.8	84.2	84.5
133	149.7	166.5	44.4	42.1	84.9	85.2
134	150.9	167.7	44.7	42.5	85.5	85.8
135	152.0	169.0	45.1	42.8	86.2	86.5
136	153.1	170.2	45.4	43.1	86.8	87.1

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
137	154.2	171.5	45.7	43.4	87.4	87.7
138	155.4	172.7	46.1	43.8	88.1	88.3
139	156.5	174.0	46.4	44.1	88.7	88.9
140	157.6	175.2	46.8	44.4	89.4	89.6
141	158.7	176.5	47.1	44.7	90.0	90.2
142	159.9	177.7	47.5	45.1	90.7	90.8
143	161.0	179.0	47.8	45.4	91.3	91.5
144	162.1	180.2	48.1	45.7	92.0	92.1
145	163.2	181.5	48.5	46.0	92.6	92.8
146	164.4	182.7	48.8	46.4	93.3	93.4
147	165.5	184.0	49.2	46.7	93.9	94.0
148	166.6	185.2	49.5	47.0	94.6	94.7
149	167.7	186.5	49.9	47.4	95.3	95.3
150	168.9	187.8	50.2	47.7	95.9	96.0
151	170.0	189.0	50.6	48.0	96.6	96.6
152	171.1	190.3	50.9	48.3	97.2	97.2
153	172.3	191.5	51.3	48.7	97.9	97.9
154	173.4	192.8	51.6	49.0	98.5	98.5
155	174.5	194.0	52.0	49.3	99.2	99.2
156	175. .	195.3	52.3	49.6	99.8	99.8
157	176.8	196.5	52.7	50.0	100.5	100.4
158	177.9	197.8	53.0	50.3	101.1	101.1
159	179.0	199.0	53.4	50.6	101.8	101.7
160	180.1	200.3	53.7	50.9	102.4	102.4
161	181.3	201.5	54.0	51.3	103.1	103.0
162	182.4	202.8	54.4	51.6	103.7	103.6
163	183.5	204.0	54.7	51.9	104.4	104.3
164	184.6	205.3	55.1	52.3	105.0	104.9
165	185.8	206.5	55.4	52.6	105.7	105.6
166	186.9	207.8	55.8	52.9	106.3	106.2
167	188.0	209.0	56.1	53.3	107.0	106.8
168	189.1	210.3	56.5	53.6	107.6	107.5
169	190.3	211.5	56.8	53.9	108.3	108.1
170	191.4	212.8	57.2	54.2	108.9	108.8
171	192.5	214.0	57.5	54.6	109.6	109.4
172	193.6	215.3	57.9	54.9	110.2	110.1
173	194.8	216.5	58.2	55.2	110.9	110.7
174	195.9	217.8	58.6	55.6	111.6	111.3
175	197.0	219.0	58.9	55.9	112.2	112.0
176	198.1	220.3	59.3	56.2	112.9	112.6
177	199.3	221.5	59.6	56.6	113.5	113.3
178	200.4	222.8	60.0	56.9	114.2	113.9
179	201.5	224.0	60.3	57.2	114.9	114.5
180	202.6	225.3	60.7	57.6	115.5	115.2
181	203.8	226.5	61.0	57.9	116.1	115.8
182	204.9	227.8	61.4	58.2	116.8	116.5
183	206.0	229.0	61.7	58.6	117.4	117.1
184	207.1	230.3	62.1	58.9	118.1	117.8

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
185	208.3	231.5	62.4	59.2	118.8	118.4
186	209.4	232.7	62.8	59.6	119.4	119.
187	210.5	234.0	63.1	59.9	120.1	119.7
188	211.7	235.3	63.5	60.2	120.7	120.3
189	212.8	236.5	63.9	60.6	121.4	121.0
190	213.9	237.8	64.2	60.9	122.0	121.6
191	215.0	239.0	64.6	61.2	122.7	122.3
192	216.2	240.3	64.9	61.6	123.3	122.9
193	217.3	241.5	65.3	61.9	124.0	123.6
194	218.4	242.8	65.6	62.2	124.7	124.2
195	219.5	244.0	66.0	62.6	125.3	124.8
196	220.7	245.3	66.3	62.9	126.0	125.5
197	221.8	246.5	66.7	63.2	126.6	126.1
198	222.9	247.8	67.0	63.6	127.3	126.8
199	224.0	249.0	67.4	63.9	127.9	127.4
200	225.2	250.3	67.8	64.2	128.6	128.1
201	226.3	251.5	68.1	64.6	129.2	128.7
202	227.4	252.8	68.5	64.9	129.9	129.4
203	228.5	254.0	68.8	65.2	130.6	130.0
204	229.7	255.3	69.2	65.6	131.2	130.6
205	230.8	256.5	69.5	65.9	131.9	131.3
206	231.9	257.8	69.9	66.2	132.5	131.9
207	233.0	259.0	70.2	66.6	133.2	132.6
208	234.2	260.3	70.6	66.9	133.8	133.2
209	235.3	261.5	71.0	67.3	134.5	133.9
210	236.4	262.8	71.3	67.6	135.2	134.5
211	237.6	264.0	71.7	67.9	135.8	135.2
212	238.7	265.3	72.0	68.3	136.5	135.8
213	239.8	266.5	72.4	68.6	137.1	136.5
214	240.9	267.8	72.7	69.0	137.8	137.1
215	242.1	269.0	73.1	69.3	138.5	137.8
216	243.2	270.3	73.4	69.6	139.1	138.4
217	244.3	271.5	73.8	70.0	139.8	139.1
218	245.4	272.8	74.2	70.3	140.4	139.7
219	246.6	274.1	74.5	70.7	141.1	140.3
220	247.7	275.4	74.9	71.0	141.8	141.0
221	248.7	276.6	75.2	71.4	142.4	141.6
222	249.9	277.9	75.6	71.7	143.1	142.3
223	251.0	279.1	76.0	72.0	143.7	142.9
224	252.1	280.4	76.3	72.4	144.4	143.6
225	253.3	281.6	76.7	72.7	145.1	144.2
226	254.4	282.9	77.0	73.1	145.7	144.9
227	255.6	284.1	77.4	73.4	146.4	145.5
228	256.7	285.4	77.8	73.7	147.0	146.2
229	257.8	286.6	78.1	74.1	147.7	146.8
230	258.9	287.9	78.5	74.4	148.4	147.5
231	260.1	289.1	78.8	74.8	149.0	148.1
232	261.2	290.4	79.2	75.1	149.7	148.8

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
233	262.3	291.6	79.6	75.4	150.3	149.4
234	263.1	292.9	79.9	75.5	151.0	150.1
235	264.6	294.1	80.3	76.1	151.7	150.7
236	265.7	295.4	80.6	76.5	152.3	151.4
237	266.8	296.6	81.0	76.8	153.0	152.0
238	268.0	297.9	81.4	77.2	153.6	152.6
239	269.1	299.1	81.7	77.5	154.3	153.3
240	270.2	300.4	82.1	77.8	155.0	153.9
241	271.3	301.6	82.5	78.2	155.6	154.6
242	272.5	302.9	82.8	78.5	156.3	155.2
243	273.6	304.1	83.2	78.9	157.0	155.9
244	274.7	305.4	83.5	79.2	157.6	156.5
245	275.8	306.6	83.9	79.6	158.3	157.2
246	277.0	307.9	84.3	79.9	159.0	157.8
247	278.1	309.1	84.6	80.2	159.6	158.5
248	279.2	310.4	85.0	80.6	160.3	159.1
249	280.3	311.6	85.4	80.9	160.9	159.8
250	281.5	312.9	85.7	81.3	161.6	160.4
251	282.6	314.1	86.1	81.6	162.2	161.1
252	283.7	315.4	86.5	82.0	162.9	161.7
253	284.8	316.6	86.8	82.3	163.6	162.4
254	286.0	317.9	87.2	82.7	164.2	163.0
255	287.1	319.1	87.6	83.0	164.9	163.7
256	288.2	320.4	87.9	83.4	165.6	164.3
257	289.3	321.6	88.3	83.7	166.2	165.0
258	290.5	322.9	88.7	84.1	166.9	165.6
259	291.6	324.1	89.0	84.4	167.6	166.3
260	292.7	325.4	89.4	84.8	168.2	166.9
261	293.8	326.6	89.8	85.1	168.9	167.6
262	295.0	327.9	90.1	85.5	169.5	168.3
263	296.1	329.1	90.5	85.8	170.2	168.9
264	297.2	330.4	90.8	86.1	170.9	169.6
265	298.3	331.6	91.2	86.5	171.6	170.2
266	299.5	332.9	91.5	86.8	172.2	170.9
267	300.6	334.1	91.9	87.2	172.9	171.5
268	301.7	335.4	92.3	87.5	173.5	172.2
269	302.8	336.7	92.7	87.9	174.2	172.8
270	304.0	338.0	93.1	88.2	174.9	173.5
271	305.1	339.2	93.4	88.6	175.5	174.1
272	306.2	340.5	93.8	88.9	176.2	174.8
273	307.3	341.7	94.2	89.3	176.9	175.4
274	308.5	343.0	94.5	89.6	177.5	176.1
275	309.6	344.2	94.9	90.0	178.2	176.7
276	310.7	345.5	95.3	90.3	178.9	177.4
277	311.9	346.7	95.6	90.7	179.5	178.0
278	313.0	348.0	96.0	91.1	180.2	178.7
279	314.1	349.2	96.4	91.4	180.9	179.3
280	315.2	350.5	96.7	91.8	181.5	180.0

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$	Invert sugar. Mg. $C_6H_{12}O_6$	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$
281	316.4	351.7	97.1	92.1	182.2	180.6
282	317.5	353.0	97.5	92.5	182.9	181.3
283	318.6	354.2	97.9	92.8	183.5	181.9
284	319.7	355.5	98.2	93.1	184.2	182.6
285	320.9	356.7	98.6	93.5	184.9	183.2
286	322.0	358.0	99.0	93.9	185.5	183.9
287	323.1	359.2	99.4	94.2	186.2	184.6
288	324.2	360.5	99.7	94.6	186.9	185.2
289	325.3	361.7	100.1	94.9	187.6	185.9
290	326.4	363.0	100.5	95.3	188.2	186.5
291	327.5	364.2	100.8	95.6	188.8	187.2
292	328.7	365.5	101.2	96.0	189.	187.8
293	329.9	366.7	101.6	96.3	190.1	188.5
294	331.0	368.0	101.9	96.7	190.8	189.1
295	332.1	369.2	102.3	97.1	191.4	189.8
296	333.3	370.5	102.7	97.4	192.1	190.4
297	334.4	371.7	103.1	97.8	192.8	191.1
298	335.5	373.0	103.4	98.1	193.5	191.8
299	336.6	374.2	103.8	98.5	194.2	192.4
300	337.8	375.5	104.2	98.9	194.9	193.1
301	338.9	376.7	104.6	99.2	195.6	193.7
302	340.0	378.0	105.0	99.6	196.2	194.4
303	341.1	379.2	105.3	99.9	196.9	195.0
304	342.3	380.5	105.7	100.3	197.6	195.7
305	343.4	381.7	106.1	100.6	198.3	196.3
306	344.5	383.0	106.4	101.0	198.9	197.0
307	345.6	384.2	106.8	101.3	199.6	197.6
308	346.8	385.5	107.2	101.7	200.3	198.3
309	347.9	386.7	107.6	102.1	200.9	199.0
310	349.0	388.0	107.9	102.4	201.6	199.6
311	350.1	389.2	108.3	102.8	202.3	200.3
312	351.3	390.5	108.7	103.1	202.9	200.9
313	352.4	391.7	109.1	103.5	203.6	201.6
314	353.5	393.0	109.5	103.8	204.3	202.2
315	354.6	394.2	109.8	104.2	204.9	202.9
316	355.8	395.5	110.2	104.6	205.5	203.6
317	356.9	396.7	110.6	104.9	206.2	204.2
318	358.0	398.0	111.0	105.3	206.8	204.9
319	359.1	399.2	111.4	105.6	207.5	205.5
320	360.3	400.5	111.7	106.0	208.2	206.2
321	361.4	401.7	112.1	106.4	208.9	206.8
322	362.5	403.0	112.5	106.7	209.6	207.5
323	363.7	404.2	112.9	107.1	210.3	208.2
324	364.8	405.5	113.2	107.5	211.0	208.8
325	365.9	406.7	113.6	107.8	211.7	209.5
326	367.0	408.0	114.0	108.2	212.3	210.1
327	368.2	409.2	114.4	108.5	213.0	210.8
328	369.3	410.5	114.8	108.9	213.6	211.5

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
329	370.4	411.8	115.1	109.3	214.3	212.1
330	371.5	413.1	115.5	109.6	214.9	212.8
331	372.7	414.3	115.9	110.0	215.6	213.4
332	373.8	415.6	116.3	110.3	216.3	214.1
333	374.9	416.8	116.7	110.7	217.0	214.7
334	376.0	418.1	117.0	111.1	217.7	215.4
335	377.2	419.3	117.4	111.5	218.4	216.1
336	378.3	420.6	117.8*	111.8	219.1	216.7
337	379.4	421.9	118.2	112.2	219.8	217.4
338	380.5	423.1	118.6	112.5	220.4	218.0
339	381.7	424.4	119.0	112.9	221.1	218.7
340	382.8	425.6	119.4	113.3	221.7	219.3
341	383.9	426.9	119.8	113.6	222.4	220.0
342	385.0	428.1	120.1	114.0	223.0	220.7
343	386.2	429.4	120.5	114.4	223.7	221.3
344	387.3	430.6	120.9	114.7	224.4	222.0
345	388.4	431.9	121.3	115.1	225.1	222.6
346	389.6	433.1	121.7	115.5	225.8	223.3
347	390.7	434.4	122.1	115.8	226.5	224.0
348	391.8	435.6	122.4	116.2	227.2	224.6
349	392.9	436.9	122.8	116.6	227.9	225.3
350	394.0	438.1	123.2	117.0	228.5	225.9
351	395.2	439.4	123.6	117.3	229.2	226.6
352	396.3	440.6	124.0	117.7	229.9	227.3
353	397.4	441.9	124.3	118.1	230.6	227.9
354	398.6	443.1	124.7	118.4	231.2	228.6
355	399.7	444.4	125.1	118.8	231.9	229.2
356	400.8	445.7	125.5	119.2	232.6	229.9
357	401.9	446.1	125.9	119.5	233.2	230.6
358	403.1	448.1	126.3	119.9	233.9	231.2
359	404.2	449.4	126.7	120.3	234.6	231.9
360	405.3	450.6	127.1	120.7	235.3	232.6
361	406.4	451.9	127.5	121.0	236.0	233.2
362	407.6	453.1	127.9	121.4	236.6	233.9
363	408.7	454.4	128.2	121.8	237.3	234.5
364	409.8	455.6	128.6	122.1	238.0	235.2
365	410.9	456.9	129.0	122.5	238.7	235.9
366	412.1	458.1	129.4	122.9	239.4	236.5
367	413.2	459.4	129.8	123.2	240.1	237.2
368	414.3	460.6	130.2	123.6	240.7	237.8
369	415.4	461.9	130.6	124.0	241.4	238.5
370	416.6	463.1	131.0	124.3	242.1	239.2
371	417.7	464.4	131.4	124.7	242.8	239.8
372	418.8	465.6	131.8	125.1	243.5	240.5
373	420.0	466.9	132.1	125.5	244.1	241.2
374	421.1	468.1	132.5	125.8	244.8	241.8
375	422.2	469.4	132.9	126.2	245.5	242.5
376	423.3	470.6	133.3	126.6	246.2	243.1

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$.	Invert sugar. Mg. $C_6H_{12}O_6$.	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$.
377	424.5	471.9	133.7	127.0	246.8	243.8
378	425.6	473.0	134.1	127.4	247.5	244.5
379	426.7	474.3	134.5	127.7	248.2	245.1
380	427.8	475.6	134.9	128.1	248.9	245.8
381	429.0	476.8	135.3	128.5	249.6	246.5
382	430.1	478.1	135.7	128.8	250.2	247.1
383	431.2	479.3	136.1	129.2	250.9	247.8
384	432.3	480.6	136.5	129.6	251.6	248.5
385	433.5	481.8	136.9	130.0	252.3	249.1
386	434.6	483.1	137.3	130.3	253.0	249.8
387	435.7	484.3	137.7	130.7	253.6	250.4
388	436.8	485.6	138.0	131.1	254.3	251.1
389	438.0	486.9	138.4	131.5	255.0	251.8
390	439.1	488.2	138.8	131.9	255.7	252.4
391	440.2	489.4	139.2	132.2	256.4	253.1
392	441.3	490.7	139.6	132.6	257.0	253.8
393	442.4	491.9	140.0	133.0	257.7	254.4
394	443.6	493.2	140.4	133.4	258.4	255.1
395	444.7	494.4	140.8	133.8	259.1	255.8
396	445.9	495.7	141.2	134.2	259.8	256.4
397	447.0	496.9	141.6	134.5	260.5	257.1
398	448.1	498.2	142.0	134.9	261.1	257.8
399	449.2	499.5	142.4	135.3	261.8	258.4
400	450.3	500.7	142.8	135.7	262.5	259.1
401	451.5	502.0	143.2	136.1	263.2	259.8
402	452.6	503.2	143.6	136.4	263.9	260.4
403	453.7	504.5	144.0	136.8	264.5	261.1
404	454.8	505.7	144.4	137.2	265.2	261.8
405	456.0	507.0	144.8	137.6	265.9	262.4
406	457.1	508.2	145.2	137.9	266.6	263.1
407	458.2	509.5	145.6	138.3	267.3	263.8
408	459.4	510.7	146.0	138.7	267.9	264.4
409	460.5	512.0	146.4	139.1	268.6	265.1
410	461.6	513.2	146.8	139.5	269.3	265.8
411	462.7	514.5	147.2	139.9	270.0	266.4
412	463.8	515.7	147.6	140.2	270.7	267.1
413	465.0	517.0	148.0	140.6	271.4	267.8
414	466.1	518.2	148.4	141.0	272.1	268.4
415	467.2	519.5	148.8	141.4	272.8	269.1
416	468.4	520.7	149.2	141.8	273.5	269.7
417	469.5	522.0	149.6	142.2	274.1	270.4
418	470.6	523.2	150.0	142.6	274.8	271.1
419	471.8	524.5	150.4	143.0	275.5	271.8
420	472.9	525.7	150.8	143.3	276.2	272.4
421	474.0	527.0	151.2	143.7	276.9	273.1
422	475.1	528.2	151.6	144.1	277.6	273.8
423	476.2	529.5	152.0	144.5	278.3	274.4
424	477.4	530.7	152.4	144.9	278.9	275.1

TABLE IV (Continued).

Copper. Mg.	Cuprous oxide. Mg.	Cupric oxide. Mg.	Glucose. Mg. $C_6H_{12}O_6$	Invert sugar. Mg. $C_6H_{12}O_6$	Lactose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$	Maltose. Mg. $C_{12}H_{22}O_{11} \cdot H_2O$
425	478.5	532.0	152.	145.3	279.6	275.8
426	479.	533.2	153.2	145.7	280.3	276.5
427	480.7	534.5	153.6	146.1	280.9	277.1
428	481.9	535.7	154.0	146.4	281.6	277.8
429	483.0	537.0	154.4	146.8	282.3	278.5
430	484.1	538.2	154.8	147.2	282.9	279.1
431	485.3	539.5	155.3	147.6	283.6	279.8
432	486.4	540.7	155.7	148.0	284.3	280.5
433	487.5	542.0	156.1	148.4	285.0	281.1
434	488.6	533.2	156.5	148.8	285.7	281.8
435	489.7	544.5	156.9	149.1	286.4	282.5
436	490.9	545.7	157.3	149.5	287.1	283.1
437	492.0	547.0	157.7	149.9	287.8	283.8
438	493.1	548.2	158.1	150.3	288.5	284.5
439	494.3	549.5	158.5	150.7	289.2	285.2
440	495.4	550.7	158.9	151.1	289.9	285.8
441	496.5	552.0	159.3	151.5	290.6	286.5
442	497.6	553.2	159.8	151.9	291.3	287.2
443	498.8	554.5	160.2	152.3	292.0	287.8
444	499.9	555.7	160.6	152.7	292.7	288.5
445	501.0	557.0	161.0	153.1	293.4	289.2
446	502.1	558.2	161.4	153.5	294.1	289.8
447	503.2	559.5	161.8	153.9	294.8	290.5
448	504.4	560.7	162.2	154.3	295.5	291.2
449	505.5	562.0	162.6	154.7	296.2	291.9
450	506.6	563.3	163.0	155.1	296.9	292.5

NEW BOOKS.

Famous Chemists. By E. ROBERTS, B.Sc. New York: The MacMillan Company.
pp. 243. Price, \$0.80 net.

The book contains very brief accounts of the lives and researches of Stahl, Boyle, Black, Cavendish, Priestley, Scheele, Lavoisier, Berthollet, Dalton, Davy, Gay-Lussac, Berzelius, Faraday, Dumas, Wöhler, Liebig, Graham, Bunsen, Hofmann, Pasteur, Williamson, Frankland, Kekulé, Mendeléeff, Perkin, and V. Meyer. The author says in the preface: "The object of this little book is to give an account of the chief work of the most famous chemists, and to indicate briefly the part played by each in the development of the science." While the names of a few of "the most famous chemists" are lacking in the list, the accounts which are given are in the main satisfactory. However, the book contains a few errors, the most serious of which are listed below.

P. 52, "Lavoisier showed that respiration is analogous to combustion." This fact had long been known. P. 59, "Chemists, up to the beginning of the nineteenth century, considered it a self-evident fact that sub-

stances combine in fixed proportions." On p. 81, it is stated that Davy established the elementary nature of iodine; it was Gay-Lussac who did this. And on p. 85, Gay-Lussac is given credit as the sole discoverer of the law which had previously been discovered by Charles. On p. 91, it is stated that Berzelius in his atomic weight work availed himself of Dulong and Petit's law. As a matter of fact, Berzelius was not well disposed towards this law. Late in his life (*Jahresbericht*, 1842, p. 6) he discussed the changes in his atomic weights proposed in 1840 by Regnault, as the result of his specific heat determinations, and accepted the further halving of his atomic weight for silver; Berzelius' original atomic weight for silver had been halved by himself many years before on the basis of Mitscherlich's Law of Isomorphism. G. MCP. SMITH.

Some Chemical Problems of To-day. By ROBERT KENNEDY DUNCAN. New York: Harper Brothers. 1911. pp. 254. Price, \$2.00.

This book like the others by Professor Duncan is of a popular character; it is written in a lively style, gives an entertaining account of some of the problems in theoretical and industrial chemistry and makes a plea for a closer relationship between chemistry and manufacture in America. He calls attention in the first chapter to a number of practical problems that it would be desirable to solve, such as the utilization of metallic cobalt, tellurium, silicon and electrolytic iron. There is need of improvement in enamels, bleaching agents, substitutes for wood, in the refinishing and recoloring of leather, in inks and shoe-blackening. The residues from paper pulp ought to be utilized, cull oranges and lemons ought to be converted into valuable substances and the western oyster ought to be improved. A hard water soap is desirable. The author says: "The many and important actual opportunities that lie everywhere at hand for applying scientific knowledge and scientific method to the manufacturing needs of men make one frankly consider why trained and earnest men should devote laborious days to making diketotetrahydroquinazoline, or some equally academic substance, while on every side these men are needed for the accomplishment of real achievement in a world of manufacturing waste and ignorance." Nevertheless he cannot be seriously opposed to scientific research as distinguished from technical research for the next four chapters deal with such theoretical subjects as "the question of the atom," "the witherward of matter," "the chemical interpretation of life" and "the beginning of things."

In the sixth chapter he considers the trend of invention as shown by the records of the Patent Office in Washington. He points out that eminent European professors like Emil Fischer, Wilhelm Ostwald and certain English university professors have taken out American chemical patents and that instead of "giving his discoveries to the world," it is much better for the man of science as well as for the public that the

discovery be patented. Some of the subjects of recent chemical patents are here discussed, such as the fixation of atmospheric nitrogen, the synthesis of ammonia, the preparation of valuable compounds from natural gas, deflocculated graphite, electric osmosis and the welding of copper upon iron.

There are chapters upon the camphor and bread-baking industries, upon the relation between chemistry and manufacture in America, on the relation of the University of Wisconsin to the State and a final chapter on the industrial fellowships that have been established at the Universities of Kansas and Pittsburgh under Professor Duncan's direction.

EDWARD H. KEISER.

Traité de Chimie générale. Ouvrage Traduit sur la 6^e Édition Allemande par A. CORVISY. Paris, 1912. Librairie Scientifique, A. Hermann et Fils. Two volumes, 20 francs each.

The comparison with the German original of a dozen pages taken here and there showed that the translation is accurate and faithful; it is also clear, direct and lucid, as we expect from the French of a master.

The invaluable work of Nernst can still be contained within the limits of a single volume, but by sacrificing something for compactness. This French edition appears in two volumes, allowing a somewhat clearer type and better spacing of lines, and presenting a very attractive page. A subject index is lacking.

The translator has added three very valuable notes: on the determination of molecular weights by measurements of osmotic pressure, on the list of radioactive elements with their constants, and on the absolute number of molecules in the unit volume of a gas.

EDWARD W. MORLEY.

Text-book of Inorganic Chemistry. By DR. A. F. HOLLEMAN. Issued in English in Coöperation with Herman Charles Cooper. Fourth English Edition, completely revised. John Wiley and Sons, New York. pp. viii + 505, 79 figures. Price, \$2.50. Cloth.

This is a new edition of Holleman's well known and admirable text, the first edition of which appeared in English in 1902. In the preface it is stated to have been thoroughly revised, many parts having been rewritten, the chapter on metal-ammonia compounds as approved by Professor Werner.

It is a good example of the text-books presenting inorganic on a basis of physical chemistry from the beginning. To many it will probably seem too condensed for use with beginners, but it is a most interesting book for more advanced students.

The order of presentation of the descriptive part is oxygen, hydrogen, water, chlorine, hydrochloric acid, the halogens, the oxygen family, the nitrogen family, the carbon family, the alkali metals, etc. At ap-

appropriate points more general topics are concisely presented, such as the atomic and molecular theories, catalysis, kinetic theory of gases, determination of molecular weights by freezing-point, boiling-point and osmotic pressure methods, chemical equilibrium and reaction velocity, electrolytic dissociation, the phase rule, valence, thermo-chemistry, determination of atomic weights, the periodic system, spectroscopy, the unity of matter, radioactivity, electro-chemistry and Werner's theory of valence.

In the opinion of the reviewer free oxygen should be represented by its formula O_2 whenever used, even before the derivation of the numeral has been explained, rather than O ; on page 34 appears the equation $2HCl + O = H_2O + Cl_2$, referring to the "oxygen of the air"; if the reader is not prepared for O_2 , the use of Cl_2 is surely illogical. The term "single decomposition" as opposed to "double decomposition" on page 40 is unusual and seems hardly justified—implying a distinction without a fundamental difference. The atomic weight of niton is given on page 405 as 2.22 instead of 222.4 as in the table of International Atomic Weights for 1912 on the inside of the end cover. Should we not distinguish between elementary substances and elements? Diamond, graphite, and amorphous carbon are elementary substances; carbon is an element.

The book offers little cause for adverse criticism, however. The language is clear, there are very few typographical errors, there is a good index, the print is good, the binding, when received by the reviewer, was defective, and became distinctly more so during inspection.

P. N. EVANS.

Handbuch der Mineral Chemie. Edited by DOELTER, *et al.* Theodor Steinkopf. Dresden. Vol. I, No. 4, Bogen 31-40. Price, M. 6.50.

The subject of the carbonate minerals is completed in this number. Those included herein are for the most part rare, and add but little to our knowledge of mineral synthesis or mineral genesis. More than half the total number of pages is devoted to silicon and the silicates. Silicate analysis by Dittrich takes up about 35 pages, and is probably as well done as could be expected in this limited space. Some important details are omitted; such, for example, as the necessity of burning the filter slowly in the silica determination to insure complete incineration, and the serious contamination of the iron-alumina ppt. by siliceous matter, if the ammoniacal solution is boiled in glass. The findings of Gooch and Austin in the magnesia determination are neither heeded nor referred to, though in the main the researches of Americans like Gooch, Hillebrand, Penfield, J. Lawrence Smith and Treadwell are given the place which their importance demands. Electric furnaces of both arc and resistance types are described by Herold. Among the types of gas furnaces in use, the Fletcher is spoken of as having the serious disadvantage of affording insufficiently high temperatures. As a matter of fact with

sufficient blast, the operator has to exercise care in working with high-melting silicates in the Fletcher furnace to avoid melting the platinum crucible! Prof. Doelter gives a few pages of general matter on the chemical peculiarities of the silicon compounds and a historical introduction to the subject of silicate synthesis, and then he proceeds to deal with bare hands with the determination of mineral melting points, to the importance of which he is thoroughly alive. The tendency to take somewhat contradictory views upon certain subjects which appear in some of his writings is here happily avoided. The statements are direct and unambiguous and as such deserve commendation. On page 629 we learn that *only a few silicates give sharp melting points*. This behavior is attributed to the peculiar viscosity of the silicates, which greatly retards the change from the crystalline to the amorphous condition, a characteristic which permits of their being overheated beyond the point at which melting begins before the process is complete. Undoubtedly there are examples of silicates like the sodium aluminium and potassium aluminium silicates (the alkali feldspars) to which should be added quartz, which present extraordinary phenomena of this sort. It is also quite possible that further study will reveal other cases of the same character, but without more knowledge than we now possess, the statement that "many other alumino-silicates belong in this class" is quite unwarranted. It is certainly preposterous to put anorthite in this class as Prof. Doelter apparently does. This phenomenon of overheating, to the possibility of which D. describes the higher points of other investigators, can be realized only to a very slight degree in the majority of silicates which have been carefully investigated. "The silicates, with some exceptions, like sodium, lithium and lead silicates do not show sharp melting points," says Prof. Doelter. True, the synthetic silicates, so far, do not melt with the same sharpness as the pure metals. It may also be true that the difference in viscosity has something to do with this, though the synthetic silicates have not yet been prepared so pure as copper, silver and a number of other metals. But the metasilicates of calcium and magnesium, diopside and anorthite (true chemical compounds) certainly melt within very narrow limits, *when pure*. Thus, Day and Sosman (*Am. J. Sci.*, 31, 341 (1911)) have recently shown that the melting points of diopside and anorthite are reproducible within 2° , while by a process of chilling and microscopic examination they have proved that no melting takes place 5° below this point. Again, on page 637, we read: "The causes of these differences (in melting-point determinations), which are quite striking, lie (1) in the difference in conception of what one calls a melting point; (2) in the difference in the exactness of methods; (3) in the difference in the size of the grains of the material to be investigated; (4) in the difference in the rate of heating. Let us revise this as follows: Differences

in melting-point determinations are due (1) to differences in the purity of material. Prof. Doelter has had long experience in the determination of the melting point of minerals, but until recent years he has always used natural minerals, and indeed at one time scouted the investigation of synthetic substances. He heats his silicates, as a rule, in quartz beakers or porcelain crucibles, stating that the vessels are little corroded, though no analytical evidence has ever been presented to prove that the melts remain pure. Now he has turned to synthetic work, but is the fact that a mineral is synthetic any proof of its purity? Apparently we are to believe so, and if a double guarantee is demanded we are told that the synthetic mixture is compounded of Kahlbaum's chemicals. Alas, poor Kahlbaum, what a burden of responsibility is thrown upon his estimable shoulders! It is perhaps not generally known to what a degree *small quantities* of impurities may affect the thermal behavior of a substance. As an example of this we may cite magnesium metasilicate, which, when pure, melts quite sharply and when cooled at a moderate rate, undercools only about 10° . Yet if 0.5% of alumina be added, the silicate may be held for an hour 50° below the melting point with but little crystallization and that of an entirely other (unstable) crystal form. (2) The thermal methods should, of course, be exact. Subjective methods may be barred without comment. The portable galvanometer with calibrated scale so commonly used to-day is a very useful instrument, but not a very accurate one; it is totally inadequate for the location or even the detection of many heat changes, but much more important is the question of the thermocouple. In ordinary furnace work this is constantly liable to contaminations which greatly lower its electromotive force, so that a calibration which consists in the observation of its reading at a single point, especially a point remote from the temperature region to which the investigation has been confined, is not sufficient to standardize the element. When investigators bring themselves to rigid conformity with these two prime conditions, it will be time to consider such secondary matters as size of grain and rate of heating which are relatively negligible, though they have a place in exact work. We may then hope to see the differences of 150° (page 632) between the determinations of the Geophysical Laboratory and those of some other investigators narrowed down to respectable limits. The application of the eutectic principle to silicate melts by J. H. L. Vogt, Doelter endorses in so far as it has to do with the quartz-orthoclase rocks, because in nature the viscosity of the magmas was reduced by water so that equilibrium could assert itself. Quite otherwise, he maintains, are the facts pertaining to the more viscous melts of the laboratory. Undoubtedly, as all will agree, equilibrium sometimes (perhaps often) fails in the silicate systems of nature as well as those of the laboratory; so it does in systems of many other substances.

Certainly a comparatively rapid cooling of silicate melts is not the best way to reach it, but to say that the phase rule can not be applied to silicate melts (pages 632 and 633) is to reject practically all the best work that has been done on the subject.

E. T. ALLEN.

Outlines of Quantitative Analysis. By W. R. LANG AND A. TINGLE. University Press, Toronto. 1911. 64 pp. Price, \$1.00.

This book is intended to be used as a guide by students in the laboratory. Pages 7 to 10 are devoted to general explanations, and to instruments, methods, and solutions for volumetric analysis. Pages 11 to 26 give 36 examples of volumetric determinations. Pages 27 and 28 give general direction for gravimetric analysis. Pages 29 to 35 give 16 examples of gravimetric determinations. Pages 39 to 64 are devoted to the analysis of 11 simple minerals and mineral products. In the space given to each example it is not possible to do much more than indicate the method to be followed, without giving detailed directions for manipulation or discussion of methods or principles. The student must depend for these on the instructor or reference to larger works or original articles, some such references being given. No attempt is made to offer explanations based on modern physical chemistry. The methods are the standard ones and are up-to-date. The minerals and products chosen for analysis are substances which the analyst is likely to meet in ordinary practice, and vary sufficiently to give the student an acquaintance with the more important separations and determinations.

WARREN RUFUS SMITH.

Papers on Pyrimidines. Edited by HENRY L. WHEELER AND TREAT B. JOHNSON. Published by Treat B. Johnson, New Haven, Conn. Price, \$2.50.

This book is a collection of the reprints of forty-eight papers giving an account of the work on pyrimidines done in the Sheffield Laboratory of Yale University prior to 1910. A twenty-four page bibliography of publications on pyrimidines, arranged chronologically, is appended. It is unnecessary to speak here of the importance of the work recorded in these papers. All who are interested in this field will find it a great convenience to have the papers collected in a single volume.

W. A. N.

Microbiology for Agricultural and Domestic Science Students. Edited by CHARLES E. MARSHALL. P. Blakiston's Son & Co., Philadelphia. 1911. pp. ix + 724, with 128 illustrations. Price, \$2.50, net.

Although this volume is the result of the combined efforts of nearly a score of agricultural scientists of the United States and Canada, a very successful attempt has been made to preserve unity of thought and expression without repetition. The book is divided into three parts, viz., Part 1—Morphology and Culture of Microorganisms. Part 2—Physiology

that such a condition is general or that it can be associated generally with a decreased content in the soil of any particular mineral substance or substances is a conclusion not sustained by the available data." In fact, no one claims that the increase of yields by fertilizers is general, for many soils do not need them. It has also long been recognized that fertilizers produce many beneficial, and even sometimes injurious, effects entirely apart from their action as plant food, hence no one would think of claiming that their effect was always and entirely due to their action as plant food. The absolute claim is the one made by the author, that they do not function in the soil as necessary additional plant food.

A chapter is next devoted to the dynamic nature of the soil, another to a valuable and interesting discussion of the film water and the relation of surface tension to the soil problem. It is here pointed out that fertilizer salts when applied to the soil lower the vapor pressure of the water, whereby a distillation of moisture to the affected points takes place from the soil below and from the air above. Thus the hypothesis is supported by another contributing factor aside from food effects.

The author next asserts that "practically every soil contains all of the rock-forming minerals" and further that if soil water is removed by a powerful centrifuge and analyzed no correlation could be found between the results and the crop yields, and that the concentrations of the solutions thus secured from saturated soils varied but little with respect to potash and phosphoric acid, regardless of textures ranging between those of sand and clay. Nevertheless, the quantities of extract thus secured were too small to make it appear probable that such analyses, as were possible, were sufficiently accurate to justify very definite conclusions.

It is then further asserted that "the concentration with respect to those constituents derived from the soil minerals will be rapidly restored whenever disturbed through absorption by plants, leaching, or otherwise." This assertion seems to be based upon experience under laboratory conditions which, however, may not apply in the soil itself. In the chapter devoted to the relation of plant growth to concentration the statement is made that "There can be no doubt, therefore, that the soil solution is normally of a concentration amply sufficient to support ordinary crop plants and is maintained at a sufficient concentration so far as mineral plant nutrients are concerned." Yet it is admitted that variations in concentration do and can result and that they probably "produce effects" upon plants. In this case the author may refer to the effect upon the turgor of the plant cell rather than to food effects.

The succeeding chapter deals with the balance between the supply and renewal of mineral plant nutrients. Following this is a most interesting and instructive chapter on the organic constituents of the soil solution. A general discussion of fertilizers including their indirect action,

and the beneficial effects of salts of manganese, etc., which are supposed not to perform the office of plant nutrients, virtually closes the argument against the plant food effects of fertilizers. The book is then concluded with a review of certain work on alkali soils.

Certain points embraced in the premises would seem to require more satisfactory substantiation before the conclusion of the work can be generally accepted. The author also begs the question, to a certain extent, at the outset by the character of his reference to "normal" condition of soils. It is also important to establish beyond question that extra amounts of mineral plant food are not needed by plants, especially at certain early stages of growth. The fact that plants can be brought to maturity in tap-water and other dilute solutions, when the latter are frequently renewed, furnishes no conclusive evidence that the renewal of mineral matter in the limited volume of water in the soil is rapid enough and sufficiently complete to meet the plant needs, especially when the minimum of water in the soil is approached which is necessary to growth, and when the root development, as in the early stages of the plant's life, is still greatly limited. Even though relatively small applications of mineral fertilizers are made they are quickly "fixed," thus enriching certain points of contact far beyond what would result if they were uniformly distributed in the entire mass of the upper eight to ten inches of soil and they may thereby become especially effective. Furthermore, it is dangerous to infer from results secured in water-culture what would transpire in the soil where so many conditions are different and so many other factors come into play.

Though a destructive agent designed apparently to minimize and relegate to the junk heap many existing theories and many of the investigations made outside of the Bureau of Soils, the book nevertheless presents a large amount of most valuable material, both by way of a review of the subjects and by original contributions. The recent chemical researches of the Bureau of Soils on the nature of the soluble organic matter of the soil deserve in this connection especial commendation. The work, though controversial and based apparently upon too broad premises, is most valuable in its suggestiveness of lines of research and is indispensable to all who are engaged in soil investigations. It is, however, to be regretted that the views of the Bureau of Soils, which have been prematurely promulgated in popular Bulletins of the Department of Agriculture, could not have been withheld for presentation only in a scientific work of this character until the chief contentions shall have been more fully established and until the hypothesis has been shown to be capable of transformation into a well supported theory. H. J. WHEELER.

Chemisch-technisches Praktikum. Uebungsbeispiele aus der chemisch-technischen Analyse für Studierende an technischen Hochschulen und Universitäten. By Dr.

Ing. Wilhelm Moldenhauer, Privatdozent für Chemie an der Technischen Hochschule zu Darmstadt. Berlin: Gebrüder Borntraeger. pp. vii + 206. Price, M. 6.

In the opinion of the author, the customary instruction in technical analysis fails in effectiveness because of lack of association with a knowledge of the technical processes or products to which the analytical work applies. He seeks to correct this difficulty by presenting a course of laboratory practice which includes the examination of typical substances of importance in the arts, and in connection with each analysis he attempts to give in outline an account of the technical processes for which the material under examination is of special importance or by which it is produced. The course is stated to represent substantially that given at the Technische Hochschule at Darmstadt and to represent an amount of work which it is claimed can be completed in a semester. The twenty-five procedures include those for the analysis of coal; drinking and feed waters; illuminating gas and that for use in balloons; spent material from gas purifiers; pyrite, nitro-sulfuric acid and fuming sulfuric acid; saltpeter; black ash; materials used in the ammonia-soda process and methods of control; fertilizers and some of their ingredients; irons and iron ores; zinc blend and zinc dust; galenite; oils, fats and waxes; soaps and glycerol; and lubricants. An introductory chapter deals with such general matters as sampling, weighing, determination of densities and the like, and an appendix contains useful tables.

The book is not one which will be of much service to the practising analyst, as it is not sufficiently comprehensive with respect either to the analytical procedures described or the discussions of the industrial applications. This is particularly true of American analysts, since many methods which are here regarded as standard methods are unmentioned. For the purposes of a course of instruction, for which it is primarily designed, the work is of considerable interest and the material and procedures are, in the main, well chosen. There is, however, an unfortunate air of finality in the treatment of the subject which would easily lead the student to suppose that the methods prescribed were practically the only ones entitled to consideration; the wet combustion method and the "color method" are, for example, the only ones mentioned for the determination of carbon. It would seem also that the author could have accomplished his purpose to give vitality to the analytical work through a knowledge of its applications more effectively if he had, in his discussions of the relevant, technical processes, pointed out more specifically why information regarding the ingredients determined was actually of significance at various points in these industrial operations. The two kinds of instructive material are presented a bit too much in layer-fashion. Nevertheless, the work is unique in its general aspects and will prove suggestive and helpful to teachers.

H. P. TALBOT.

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ELECTROLYTIC DISSOCIATION.¹

BY SVANTE ARRHENIUS.

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I received last year an invitation to come over here and give the Silliman lectures in New Haven. It is a very great honor to receive this invitation, and only the most prominent men have given these lectures in the past years. It was, therefore, with great pleasure that I accepted this invitation, and especially it was something romantic to lecture just in that place, where Willard Gibbs had lived and worked. I also had repeated opportunity in my lectures there of pointing to the extraordinarily great achievements of this forerunner in science. He was a great master in mathematics, and he developed his theories chiefly from a mathematical point of view, and hence they were, in a very high degree, generalizations, much more so than anything written before that time; but, for the same reason, they were also very difficult to follow. It was necessary to use a high degree of abstraction to understand these notions which he had introduced, and therefore very few of the chemists could realize the very great importance of his work. He came before Helmholtz, for Helmholtz about eight years later wrote on the same subject; Helmholtz was the great mathematician of his time, and still one must say that he took up only a small part of that which Willard Gibbs had achieved. And Helmholtz had the same fate as Willard Gibbs; he wrote in a very abstract manner, and very, very few paid attention to that work.

His work of 1882 was too general still, and it was only after van't Hoff, in 1886, had found a simple rule, connecting solutions with gases, that people who were not so great and prominent mathematicians as these two heroes could have a grasp of the great importance and of the

¹ The Willard Gibbs Address, delivered before the Chicago Section of the American Chemical Society, May 12, 1911.

wide scope of the work of these two, and especially of that of Willard Gibbs. And shortly after, Ostwald also translated the latter's work into German, and thereby made it available for the great public which had not had it before, because it was printed in the transactions of the Connecticut Academy, which are not very widely read, and can scarcely be obtained in the common libraries.

Now, after I had this great honor to be, in a certain degree, connected with the place where Willard Gibbs had worked, I came here to take this great honor, again connected with his name, and I must say it is the greatest honor that can be conferred upon me and it touches me more than anything else could do. I have, according to the statutes regarding this medal, to give an address regarding the subject for which it has been given. I must say that Dr. Smith has spoken so eloquently on that before, that it will be a great trouble to me to try to make it better, and I fear I will not be able to do that. I may nevertheless perhaps appeal to your kind interest by telling some of my personal dealings and views of that time.

"There is nothing new under the sun"—I believe it was King Solomon who said that, and it is true, absolutely so, to-day, and will remain so; there were some forerunners also regarding the dissociation of salts into their ions, such as sodium chloride into sodium and chloride ions in solution. It had been found that if we investigated the physical properties, especially of different salts in their solutions, if we took them in so-called equivalent proportions in the same quantities of water, then these properties show a very remarkable degree of regularity, they are called additive; they behave absolutely as if the properties could be described as the sum of the properties of the parts of the salt, at that time called radicals, now called ions, so that the properties could always be ascribed, as due for one fact to the one part of the salt, and for another fact to the rest of the salt, and then for the rest due to the solvent. For instance, if we have a solution in water, then the properties of the water are manifest, its chemical properties for instance, but they are not so very remarkable. But regarding the rest of the properties of the solution, the salts behave as if composed of two parts, two different things, one called the positive and the other the negative ion or radical, and the properties of any one of these radicals are always the same; thus all sodium salts contain the ion sodium—and this sodium ion has always the same properties. It may be combined with any one of the very great number of other radicals, negative radicals, chloride ion, bromide, sulfate ions and so forth. There was a difficulty—there are nearly always difficulties—and when these difficulties are explained, they give the best confirmation of the correctness of our ideas. It was so here; there were exceptions, a great number of exceptions, and therefore it was only the most sanguine of the investigators

who dared to state that these properties had just that character I told of. For instance, ammonia is always an exception; water is an exception; and so forth. We know now, afterwards, why they are exceptions. They must be exceptions because they are not torn asunder, their molecules are not ionized in a sensible degree. We could have stated their exceptional behavior before, but we knew no ground for it, but now we can say they are exceptions, because they do not conduct electricity. The property of conducting electricity is due mainly to ions or radicals, which are free; those substances which dissociate in solution into two parts, one positive and one negative, conduct electricity; and only those. That is the general rule. Now, it is very easy to investigate in advance which substances do not conduct electricity and then they are excluded absolutely from the substances presenting additive properties. If we exclude just those non-electrolytes, then the regularities I tell of are absolutely clear, although they could not be understood before the dissociation theory was developed.

The men who in past times had been impressed by these regularities were especially the Frenchman, Valson, and another Frenchman, Raoult, but they never dared to express the idea that the two parts of a molecule were free, absolutely free. They said that the sodium and the chlorine retained, in part, their properties in a solution of sodium chloride. That is all. They always said they are combined, but still retain a certain part of their individuality. But they could not arrive at the hypothesis of dissociation, because there were so many exceptions. They were the forerunners on the practical side, the experimental side, but there are other forerunners, more interesting and more wonderful, on the theoretical side. In France there was a physical chemist at the beginning of the last century who must have been among the most intelligent men in the world. He was not recognized as much as he merited; his name was Gay-Lussac. He had read some works of Berthollet and tried to explain some of the experiments which Berthollet cited, but in a different manner from that of Berthollet. If we mix sodium sulfate with barium chloride, we obtain barium sulfate, and sodium chloride remains in the solution, whereas barium sulfate precipitates out. This is a familiar process to chemists. The reason why barium sulfate is precipitated out, Berthollet said, was because the molecules have, so to speak, a feeling that if barium sulfate is formed, then it gives a precipitate, and all precipitates tend to be formed. Of course, this feeling of the molecules of what would happen is something very anthropomorphic and not very scientific; still Berthollet was one of the most prominent scientists of his time. It was an instance of what is called predisposing affinities. And it is one of the merits of the dissociation theory to have thrown light upon what these mystic predisposing affinities are.

Now, Gay-Lussac said there is no predisposition for anything, but that if we mix sodium sulfate with barium chloride, then there are always formed the two salts, sodium chloride and barium sulfate. All the combinations of the two positive ions, namely sodium and barium, with the two negative ions present, sulfate-ion and chloride-ion, occur, and nearly in the same degree. All of the possible combinations are formed. Now, barium sulfate will be precipitated and it does not react any more with the other salts, so these other salts are not formed again; but new barium sulfate may be formed and that precipitates anew, and goes out of action, so that new quantities of this salt are formed, until the process is completed. If it remained in the solution, it would react with the others and be transformed back into the other possible combinations, but just because it disappears, it cannot react with the others, and the process goes only in that one direction.

These ideas are, perhaps, a little abstract, but they are of the greatest interest, for they are more than eighty years old. They were expressed in 1839. And later on, in 1857, Williamson expressed absolutely similar ideas, and the same was the case with Clausius, the German mathematical physicist. Clausius came to this conclusion from quite different considerations. He did not care at all for chemical compounds; he was not familiar with them, but he investigated the electrical conductivity of salts in solution. And it was known that if one let an electric current pass through a solution, then that solution is electrolyzed, as it is called, that is, the two parts of the salt which were called radicals, and which are now called ions, are separated from each other, and are set free at the so-called poles, that is, at the two places at which the current enters and leaves the solution. And Clausius drew attention to the circumstances which had been proved by many an experimenter—(he, himself, was not an experimenter at all)—namely, that the slightest electric force is able to tear asunder these two ions from their compounds. He concluded that the ions must be free, because they are separated from each other by the least force, since, if they were held together by a finite force, it would not be possible for the least electrical force to tear them asunder. But he said: "Perhaps it is only an extremely small fraction which behaves in that manner," and thereby he diminished the value of his conclusion. It must be said that Gay-Lussac was the first who found what was the truth; what we now regard as the truth. Perhaps it is better to say that these contributions of Clausius, Williamson, Gay-Lussac, Valson and Raoult did not carry conviction on account of the antagonism against the view that common salt, which all people know, is dissociated, as it is called, that is, is torn asunder into its two parts, namely, sodium and chlorine. This idea seemed absolutely impossible; it could not be accepted. Every one knows that if we dissolve salt in water, the solution

has a salty taste, but it has not at all the properties of sodium; for sodium is a metal and is not soluble in water, except in the form of the hydroxide. Further, it has not at all the properties of common chlorine; because common chlorine gives a very disagreeable odor to water, and also a green shade to its color, and tastes extremely disagreeable and is poisonous. It is clear that if sodium chloride is dissociated into sodium and chlorine in the water, it must be something else than the common chlorine and common sodium, but this conclusion seemed hard for most chemists. But we know now very well that if you have phosphorus, for instance, you can have it at least in two different modifications. One is yellow phosphorus, it burns very easily, is very disagreeable to smell and is very poisonous; the other is red phosphorus, which is not poisonous, does not emit vapors or a bad smell, and is dark red in color, in contradistinction to the yellowish color of yellow phosphorus. The two substances seem to be as different as possible. Another case which is very familiar is that of the diamond and common carbon; they have different properties, and still it is carbon in the two cases.

Why should not sodium behave in two different manners? There is another dissimilarity in that case, namely, that the common sodium is not charged with electricity, and that the sodium, which is dissociated from the chlorine in the sodium chloride solution, carries an enormous quantity of electricity, and that may give it wholly different properties. In reality, we may say that if these difficulties are still not wholly overcome, they are not absolutely insurmountable difficulties. We may say that it is possible, and it is true, that ionization of sodium chloride forms another sodium than the common metallic sodium. But there is much work to be done still in that line, until we clearly understand it, and this work will probably throw much light on the electrical side of the question.

I had to work out a thesis in order to get a doctorate; that was in 1882—I had come so far then. The opportunities for working it out in my home university, Upsala, were not favorable, therefore I went to Stockholm. Thereby I came under the influence of the great electrician, Edlund, who had a very great diversity of interests, and I only wish to say that probably it is due to him that I have been interested in very different things. For he worked on the *aurora borealis*, and on the theory of electricity, on electric currents, on the electric arc, and so forth. He also had a great number of practical interests and was president of the Polytechnic Institute in Stockholm. When I came to him, he did not encourage me very much to continue with chemical ideas, because he did not understand them very well. He was a pure physicist, but I had some ideas of my own. My teacher in chemistry, Cleve of Upsala, a very renowned chemist, had lectured on organic chemistry, and he always

said cane sugar has the formula $C_{12}H_{22}O_{11}$, or some multiple of that, probably some very high multiple, and no one could solve that question, he said. I thought that it would be of great interest if one could solve that question, for just such things will promote science and knowledge very much, which are said to be impossible. As you know, the determination of molecular weights plays the most fundamental role in chemistry, and I thought, perhaps I can apply electrical methods in solving that question. It was often said, at that time, and is said even now, that electricity is the source of all phenomena, so that its application might solve all questions, and overcome all difficulties. I tried that, but did not succeed; but at the same time, Raoult, in France, succeeded by determining the freezing points of solutions. I did not know his results, but I continued and came to the investigation of the conductivity of solutions. There was already then a large amount of work in that line and my contributions were only a small part of what was known. But my great luck was that I investigated the conductivity of the most dilute solutions. In these dilute solutions the laws are simple compared with those for concentrated solutions, which had been examined before. It was then easy to find that the irregularities, which came in every step with concentrated solutions, disappeared. The whole thing was very simple, but it was necessary to believe that the conducting molecules which, according to Clausius, were dissociated, that these conducting molecules were the whole part of the dissolved salt in this high dilution. I knew my professors in Upsala too well and found that it would be impossible to get them to believe that. Therefore, if I had made such a statement in my doctor's thesis, it would not have been approved, so that I would have had to work on a new thesis before I could be nominated doctor. [Applause.]

Therefore, I did not say that there is a nearly total dissociation of salts in their highly diluted solutions, but I said that the salts consist of two different kinds of molecules in solutions, the one inactive—this expression did not look so dangerous—and the other active. These later conduct electricity, and the others, the inactive ones, do not. In the highest dilution all molecules are active, and I said further that the molecules which are active are in the state described by Clausius; he was a great authority, therefore it could not be regarded as unwise to share his ideas. Interesting as the electrical conductivity is, it seems of a secondary interest from a chemical point of view. But a study of Berthollet's work on thermochemistry showed me that those acids which conduct electricity the best are also chemically the strongest and always displaced the weak acids which do not conduct electricity or only conduct it poorly. With different acids the differences of conductivity are such as one to one million, in many cases. Therefore the determination of

their order regarding conductivity is very exact. It was now quite clear to me that there were no exceptions to the rule that, of two acids, that which had the better conductivity in equivalent solutions in a given solvent was also the stronger acid. The next step was also quite clear: the active molecules, which are active in regard to electricity, are also active in regard to chemical properties, and that was the great step. I might say that I am invited to the Chemists' Club of New York on the 17th of this month. That was because I told them I got that idea in the night of the 17th of May in the year 1883, and I could not sleep that night until I had worked through the whole problem. [Laughter.]

Now, after that day, I was very certain that I had made an important step, and I worked out one line after the other, in detail, and then came to new conclusions. Every one knows that water may be regarded as an acid, though a very weak one; therefore, if I have an acid, for instance, nitric acid and water, and let them compete for a base, for instance, sodium hydroxide; then the nitric acid, strong as it may be, cannot take all the sodium hydroxide, but must leave a very small part to the water; that is so-called hydrolysis.

It was very easy to work out from these considerations a theory regarding the hydrolytic activity, and I found that it agreed very well with experience, according to Berthollet's work.

These conclusions were formed with the help of the book of Berthollet, which contained everything regarding equilibrium. And then there was another thing: all acids in reacting with the same base give the same heat of neutralization; for one equivalent 13,500 calories. That is directly true only for strong acids with strong bases, for example, if I take sodium hydroxide, which is a strong base, and nitric acid, a strong acid. If I go to the weak acids I find small deviations, and if I take water I find no evolution of heat at all. What could now be the cause of this difference? It was clear that it was due only to their different degree of activity; and, therefore, I said, if I mix an absolutely active, that is, an extremely dilute, strong acid and a similar base in equivalent quantities, the same quantity of heat is always evolved. The base may be any base and the acid may be any acid. When strong acids and strong bases react, water is formed, and the heat which is evolved is simply the heat of formation of inactive water from absolutely active water. For if the water formed had been absolutely active, we should have had no heat effect at all. The difference found in neutralizing weak acids is just due to the heat of transformation of the inactive molecules of the acids into active ones. The heat of neutralization of strong acids and strong bases is the heat of combination of the ions of water, hydroxide and hydrogen ions, when inactive water, that is the common H_2O , is formed from them.

Then I arrived at another conclusion, namely, that if two electrolytes

react upon each other, they give only reactions of the ions and do not give anything else. For instance, potassium ferrocyanide, which contains potassium, iron, and carbon and nitrogen in the form of cyanogen, does not give reactions of iron or cyanogen, for these ions are not the ions of this salt; but its ions are potassium and the rest of the molecule. In all cases the one ion is the metal, and the other ion is the rest of the molecule. And this rest is not iron or cyanogen and therefore the potassium ferrocyanide does not show any reaction of iron or cyanogen. As it was called before, the "type" of the salt was "conserved" in this case, the "type" of ferrocyanides. So, if we may allow potassium ferrocyanide to react on another salt, then always a ferrocyanide, that is, a salt of the same type, is formed. This "conservation of types" could not be explained before. I had, in this manner, deduced a rather great number of different properties which had not been explained before; but I must say that this circumstance made no very great impression upon my professors in Upsala. [Laughter.]

I came to my professor, Cleve, whom I admire very much, and I said: "I have a new theory of electrical conductivity as a cause of chemical reactions." He said: "That is very interesting," and then said "Good-bye." He explained to me later, when he had to pronounce the reason for my receiving the Nobel prize for that work, that he knew very well that there are so many different theories formed, and that they are all almost certain to be wrong, for after a short time they disappear; and, therefore, by using the statistical manner of forming his ideas, he concluded that my theory also would not exist very long. [Laughter.]

I was not very content with that opinion, and then I thought, in foreign countries there are such prominent scientists, they might look at it differently; it might appeal to them. Then I wrote to Clausius, and said: "What do you think of that?" I wrote to Ostwald—he worked on the same line. I wrote to Thomsen. I received friendly answers from most of those scientists, and they were very glad to make my acquaintance, and so on, but it was not very much more. [Laughter.] The only exception was Ostwald, and he describes, himself, how it was that he got on the same day this dissertation, a toothache, and a nice daughter, and that was too much for one day, and the worst was the dissertation, for the others developed quite normally. But this bulky dissertation was very hard for him, and he said there were indications that some of its parts were not quite in order. There were some unfamiliar expressions and sanguine ideas, but, finally, he found it still might be good to look into, if it was true. He had a great number of acids, which he had investigated regarding their chemical reactivity, that is, regarding their chemical strength in catalytic reactions, and then he investigated them in regard to their conductivity, which was done very rapidly. He found

that their chemical activity and their electrical conductivity were nearly proportional to each other. Then he came to me to see me personally, and spoke with me, and we had some very pleasant days together, and then we made plans regarding the development of the whole of chemistry. Everything seemed to us so regular and fine, and we have really developed that program for the most part; but I must say that the reality has been much better than we believed at that time.

Then Ostwald, of course, visited my dear friend and teacher, Cleve. Ostwald spoke to him one day in the laboratory. I came a little later. I was not expected, and then I heard Cleve say: "Do you believe sodium chloride is dissolved into sodium and chlorine?" "In this glass I have a solution of sodium chloride; do you believe there are sodium and chlorine in it?" "Do they look so?" "Oh, yes," Ostwald said, "there is some truth in that idea," and then I came and the discussion was at an end. I was very sorry for that.

After Ostwald's visit to Cleve, I was nominated privatdozent of physical chemistry, in the autumn. Two years later I went to Ostwald in Riga to work. The work was very easy at the beginning; I collected much material and wrote it out a little later in four parts. After the visit to Riga I went to Kohlrausch, in Würzburg, and to Boltzmann, in Graz, and I visited van't Hoff's laboratory, so that I had a good schooling at that time. Everywhere I went, I worked further on the same lines. Then, when I was in Würzburg, I received a memoir of van't Hoff's, in which he had given the theory of Raoult's work regarding the freezing point, of which I spoke in the beginning. After having read this memoir it was quite clear to me that I might dare to say that all these substances which are active, that is all electrolytes, consist of two molecules, and not of one; that is, sodium chloride is composed of two molecules, the sodium ion and the chlorine ion. Then the theory of electrolytic dissociation was expressed without any restriction (1887). I had then a three-fold basis for my conclusion, the chemical one and the electrical one, and then the thermodynamical one, regarding the freezing point. On a foundation of three points you may construct a very solid building. The first publication of this hypothesis came into a report of the committee appointed by the British Association for investigating the conductivity of electrolytes. I wrote directly on this question to Ostwald. He did not understand me—I must have written a little rapidly. But later on I published the theory in a more elaborate form, and then its importance was clear to Ostwald, to van't Hoff, and many others.

I came to van't Hoff in 1888. On the way I visited Kiel—midway between Stockholm and Amsterdam—van't Hoff was at Amsterdam at that time—and then I spoke with Planck; he was very much interested in this subject, and he said: "I agree wholly with you, but there is a diffi-

culty. If I consider the conductivity of copper sulfate, I may calculate how great a part of that salt is dissociated and then this part must conform to the law of equilibrium which was announced by Guldberg and Waage. The difficulty is that my calculations do not agree with that law." He asked me if it was possible to suppose that this discrepancy was due to the circumstance that the equilibrium was not reached immediately after the solution. I said that I supposed there was no hope to help it out by such an hypothesis. Then I came to Amsterdam and when I saw van't Hoff, he said: "The dissociation theory is very good, but can you get it to accord with the law of Guldberg and Waage? I have calculated the conductivities of potassium chloride; they do not agree." Then I said to him: "Yes, that is as you say, but you ought to try the calculation with acetic acid; for with acetic acid you can change the degree of dissociation in the proportion of 1 to 100, but with the salt you cannot change it more than in a proportion of 3 to 4. Of course, you must, if you want to see if a rule is true, take the greatest variation possible." He said: "That is true, please sit down and calculate it yourself" and he gave me a logarithm table and I sat down and the result looked very well, and I showed it to him, and I said: "You see that is not so bad." He was very much interested; but he wished to have a better agreement. He said to his assistant Reicher: "You must make absolutely pure acetic acid and some other acids. I will need them." Reicher did not understand why van't Hoff needed the acids. He distilled them, but van't Hoff was not content until after some weeks of hard work. The measurements on the new, pure preparations agreed perfectly with the theory of Guldberg and Waage. During this time he received a paper in the *Zeitschrift für physikalische Chemie*, and in it Ostwald announced that he had found that the said rule holds, and therefore it is called "Ostwald's law of dilution." You will see from this example that the idea was, so to speak, in the air. Ostwald worked on it and Planck and van't Hoff worked on it simultaneously; Ostwald was the editor of the *Zeitschrift*, and used the opportunity to publish it first. He made, at first, no new, more accurate experiments, as van't Hoff did, but was content with his old figures. Later, he made a great number of new determinations; he found the law of equilibrium to be true in a very much higher degree than this law had been proven before, for gases. After this important discovery, the dissociation theory won a great number of adherents; but not all agreed with us. Every time I came to Berlin, where the young privatdozents subject scientific novelties to a severe criticism, they said: "The dissociation theory is not so bad, but perhaps it is not quite in order, and Helmholtz will fix it up for you." I spoke to Helmholtz and he didn't say so himself. It was his assistant who believed they understood science much the better. When I came to Erlangen, I spoke with Wiedemann, and he said: "It is

very interesting, of course, but you have not found the real cause of the things in question. I know what this cause is, it is the internal friction, and I hope to show it to you;" whereupon I answered: "Yes, I am thankful for that, but the more, the earlier you publish your ideas." Unfortunately, he has not done it yet, and that was twenty years ago. After some years, our opponents did not attack us any more, but still they showed a passive resistance, which all of you know is much more difficult to conquer than an active one. All of them hoped that some one would come to demonstrate that we were on the wrong path. This situation became too long and tiresome for Ostwald. He said: "Let us attack them, that is the best method." He wrote very severe criticisms of the opponents' memoirs in his journal, and he said openly that they did not understand anything regarding physical chemistry. Thereupon the opponents gave their assistants and other pupils, who were going to make investigations, subjects to treat of which they hoped would show that we were not right, and said that we were unable to explain them. But, in reality, it was always easy to find an explanation founded on the new theories of solutions, whereas no explication was given from the other side. In that manner, from our own side and from the opposition, a great deal of material favorable to the new theories was soon collected.

There were two other favorable circumstances for the progress of the dissociation theory. At that time Ostwald's great treatise on general chemistry was published, in which he used the dissociation theory. The other favorable circumstance was that Ostwald opened in Leipsic the only laboratory in the world for physical chemistry, and there came people from all nations of the world to be initiated in the new views. The smallest number of them were Germans. The Americans were very many. Ostwald was a genius. He transferred his enthusiasm for the great work to his pupils and they went out in different parts of the world and worked on physico-chemical problems, and applied the theory of van't Hoff and the dissociation theory in the explanations of their experiments. So it came about very rapidly that the new dissociation theory was in the majority and not in the minority, as before. I am glad to say that this work continues still to-day, and that especially Americans are working on the old classical lines; here are a great many laboratories where the old traditions are prevailing, more than in any other part of the world, even in Germany. Van't Hoff is, I am very sorry, dead, and Ostwald has left chemistry and gone into other branches of science, and still more of philosophy. Now the dissociation theory is brought to a certain degree of completeness—certainly there is much left to do in it—and we treat with a very great degree of accuracy a very great number of questions regarding solutions. Therefore, the time has come for the application of the theory of solutions. Solutions play the most important role in

the world; therefore the alchemists said that there is nothing which acts chemically but solutions. Solutions fill the oceans, solutions are running in our veins and solutions form the chief part of all organisms; life is bound to solutions, as well as chemical reactivity. In the broad sense of the word, the terrestrial and the celestial bodies chiefly consist of solutions, inasmuch as their chief parts are mixtures of different fluid bodies. Why should we not apply what we found regarding solutions to the different interesting problems regarding these bodies. By the application we already have cleared up fundamental chapters in different sciences, and especially in the field of physiology and biology. These applications have been of the greatest interest, and even in that line extremely good work is carried out here in America at the present time; and I have the greatest respect for and expectations from just that work, for it is clear that biology will be the chief science or the most practical science, I may say, of the coming time. It regards life, and we are living organisms, and that is our most special property; and therefore physiology, or the science regarding life, will have the greatest influence of all the sciences upon the principle of life and upon the development of humanity.

I have, perhaps, spoken too broadly regarding all of these questions which have lain so near to me, and I therefore will conclude my remarks. I only wish to say that if my dear friend, Mr. Mather, has said that I perhaps do not know that I am a member of the Society, he is very badly informed, for every month I receive four very valuable publications from here, which I read with the very greatest interest. Especially are they valuable for me because they record in a great number of cases the, for Americans characteristic, very practical treatment of the problems attacked. Mr. Mather said I am the first of the honorary members, and that is due to my great luck in having a name beginning with "A."

Now, in receiving this medal, struck in honor of our great master Willard Gibbs, I wish to express the hope that very many members of this Society, and colleagues of mine in this case, shall receive this medal in the coming years.

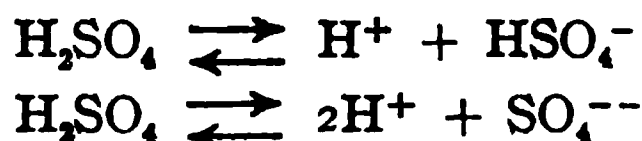
I thank you very heartily. [Great and prolonged applause.]

THE CONCENTRATION OF HYDROGEN ION IN SULFURIC ACID.

BY RICHARD C. TOLMAN AND LUCIEN H. GREATHOUSE.

Received February 10, 1912.

Sulfuric acid may dissociate according to either or both of the reactions:



Since its method of dissociation is unknown, it is impossible to calculate,

from conductivity measurements alone, either the degree of dissociation of the acid or the concentration of any of the ionic substances produced.

It occurred to the authors that the concentration of hydrogen ion in sulfuric acid could be most easily determined by the use of an indicator. The method consists in finding a solution of hydrochloric acid which imparts the same color to a definite concentration of indicator as the sulfuric acid under consideration.¹

We may consider an indicator as a weak acid which ionizes according to the reaction



the undissociated acid and its ion differing in color.

The hydrogen ion concentration of the solution in which the indicator is present will determine the degree of ionization of the indicator, and hence indirectly its color. If we find a solution of hydrochloric acid which gives the same color with the same amount of indicator as the solution of sulfuric acid under consideration, the two presumably have the same concentration of hydrogen ion which can be calculated for the hydrochloric acid from conductivity data.

Experimental.

Four dyes were finally chosen for use as indicators and were made into stock solutions of the following suitable composition:

1. 0.05 g. malachite green, 5 cc. alcohol, 95 cc. water.
2. 0.0125 g. methyl violet, 2½ cc. alcohol, 97½ cc. water.
3. 0.0166 g. tropäolin oo in 100 cc. 50% alcohol.
4. 0.05 g. methyl green, 100 cc. water.

Approximately 0.2 *N* solutions of sulfuric, hydrochloric and nitric acids and of barium hydroxide were prepared and standardized. The acids were all titrated against barium hydroxide, and this in turn titrated against succinic acid. Furthermore, independent determinations of the strength of the sulfuric and hydrochloric acids were made by precipitation of barium sulfate and silver chloride. The various standardizations were in satisfactory agreement.

Indicator was added to solutions of 0.2 *N*, 0.1 *N* and 0.05 *N* sulfuric acid and the color compared with that found in a series of differently concentrated solutions of hydrochloric and nitric acids, which were prepared by dilution from 0.2 *N* acid. The comparisons were made on a white background in Nessler tubes which had a depth of approximately 17 cm. to the 100 cc. mark. For the 0.2 *N* and 0.1 *N* acid, 50 cc. of the solutions were taken and 0.1 cc. of the indicator solution added. For the 0.05 *N* acid, 100 cc. of solutions were taken and 0.2 cc. of indicator solution added.

¹ Indicators were first systematically used for determining hydrogen ion concentration by Friedenthal, *Z. Elektrochem.*, 10, 119 (1904). See also Salm, *Z. physik. Chem.*, 57, 471 (1907).

Malachite green and methyl violet were found to be sensitive indicators in 0.2 *N* and 0.1 *N* solution, methyl green and tropäolin oo in 0.05 *N* solution.¹ The indicator was added from a buret provided with an automatic stopcock, which permitted the rapid delivery of 0.1 cc. portions. Since there is a tendency for the color of the solutions to fade, the solutions to be compared were all placed in the Nessler tubes and the indicator added to them in quick succession. The comparisons were made at room temperature, approximately 24°.

Experimental Results.

The results of the experiments are given in Tables I–III. The first column in the tables states the concentration of comparison acid whose color

TABLE I.—COLOR COMPARISON WITH THAT IN 0.2 *N* (× 1.0174) H₂SO₄.

Concentration of comparison acid.		Color in comparison acid.			
		Malachite green.		Methyl violet.	
		HCl.	HNO ₃ .	HCl.	HNO ₃ .
0.150 × (1.0033)	0.150 × (1.0121)	Greater
0.140 × (1.0033)	0.140 × (1.0121)	Greater	Greater
0.130 × (1.0033)	0.130 × (1.0121)	Slightly greater	Greater	Greater	Greater
0.120 × (1.0033)	0.120 × (1.0121)	Less	Slightly less	Less	Slightly less
0.110 × (1.0033)	0.110 × (1.0121)	Less	Less	Less	Less
Conc. HCl (1.0033) or HNO ₃ (1.0121) equivalent to 0.2 <i>N</i> H ₂ SO ₄ (1.0174)...		0.1275	0.1225	0.1250	0.1225
Concentration HCl or HNO ₃ equivalent to 0.2 <i>N</i> H ₂ SO ₄		0.1257	0.1218	0.1233	0.1218
Concentration hydrogen ion.....		0.111	0.108	0.109	0.108

TABLE II.—COLOR COMPARISON WITH THAT IN 0.1 *N* (× 1.0174) H₂SO₄.

Concentration of comparison acid.		Color in comparison acid.			
		Malachite green.		Methyl violet.	
		HCl.	HNO ₃ .	HCl.	HNO ₃ .
0.080 × (1.0033)	0.080 × (1.0121)	Greater	Greater
0.075 × (1.0033)	0.075 × (1.0121)	Greater	Greater	Greater	Greater
0.070 × (1.0033)	0.070 × (1.0121)	Same	Slightly greater	Same	Slightly greater
0.065 × (1.0033)	0.065 × (1.0121)	Less	Same	Less	Slightly less
0.060 × (1.0033)	0.060 × (1.0121)	Less
Conc. HCl (1.0033) or HNO ₃ (1.0121) equivalent to 0.1 <i>N</i> H ₂ SO ₄ (1.0174)...		0.0700	0.0662	0.0700	0.0675
Concentration HCl or HNO ₃ equivalent to 0.1 <i>N</i> H ₂ SO ₄		0.0690	0.0659	0.0690	0.0672
Concentration hydrogen ion.....		0.0620	0.0597	0.0620	0.0609

¹ For solutions as dilute as 0.005 *N* dimethylamidoazobenzene was the most suitable indicator tried, but even that lacked great sensitiveness.

TABLE III.—COLOR COMPARISON WITH THAT IN 0.05 *N* (1.0174) H_2SO_4 .

Concentration of comparison acid.		Color in comparison acid.			
		Tropæolin oo.		Methyl green.	
		HCl.	HNO_3 .	HCl.	HNO_3 .
0.0425 \times (1.0033)	0.0425 \times (1.0121)	Greater	Greater
0.0400 \times (1.0033)	0.0400 \times (1.0121)	Greater	Same	Slightly greater
0.0375 \times (1.0033)	0.0375 \times (1.0121)	Greater	Greater	Slightly less	Same
0.0350 \times (1.0033)	0.0350 \times (1.0121)	Same	Same	Less	Less
0.0325 \times (1.0033)	0.0325 \times (1.0121)	Less	Less	Less	Less
Conc. HCl (1.0033) or HNO_3 (1.0121) equivalent to 0.05 <i>N</i> H_2SO_4 (1.0174)...		0.0350	0.0350	0.0394	0.0381
Concentration HCl or HNO_3 equivalent to 0.05 <i>N</i> H_2SO_4		0.0345	0.0348	0.0389	0.0379
Concentration hydrogen ion		0.0315	0.0319	0.0356	0.0347

was contrasted with that of the solution of sulfuric acid in question and the other columns state whether the color of the comparison acid corresponded to a greater or a less hydrogen ion concentration than that of the sulfuric acid.

The results of the experiments are summarized in the lower part of each table. The first line states the concentration of comparison acid decided on as having the same color as the sulfuric acid used. The second line states the concentration of comparison acid having the same color as sulfuric acid of exact normality, and the third line states the hydrogen ion concentration of this strength of comparison acid.

The following tabulation indicates the conventions made in deciding what concentration of comparison acid would have the same color as the sulfuric acid:

Color shown by successive samples of comparison acid, contrasted with color of H_2SO_4 .	Equivalent concentration chosen as that which showed
Greater—same—less	Same color
Greater—less	Less color + $\frac{1}{2}$ conc. interval
Slightly greater—less	Less color + $\frac{3}{4}$ conc. interval
Slightly greater—same—less	Same color + $\frac{1}{4}$ conc. interval

The concentration of comparison acid isohydric with sulfuric acid of exact normality was calculated by simple proportion from the normality factors of the two acids. The concentration of hydrogen ion in the comparison acid was calculated from the conductivity data of Kohlrausch at 18° using the values for λ_0 determined by Noyes and Sammet¹ and Noyes and Kato,² 396 for hydrochloric acid, 392 for nitric acid.

¹ THIS JOURNAL, 24, 944; 25, 165 (1902–3). *Z. physik. Chem.*, 43, 49–74 (1903).

² Carnegie Institution of Washington, Publication No. 63. THIS JOURNAL, 30, 318 (1908).

TABLE IV.—RATIO OF HYDROGEN ION CONCENTRATION TO FORMAL CONCENTRATION
H₂SO₄.

Formal concentration.	Indicator method, approx. 24°.	Conductance and transference, 25°.	Picric acid expts., 25°.
0.100	1.11	1.05–1.16	1.04
	1.08		
	1.09		
	1.08		
0.050	1.24	1.13–1.24	1.10
	1.19		
	1.24		
	1.22		
0.025	1.26	1.23–1.35	1.20
	1.28		
	1.42		
	1.39		

Conclusions.

From an examination of the last lines in Tables I–III, it will be seen that the different acids and the different indicators lead to approximately the same values for hydrogen ion concentration in sulfuric acid. Small differences between the values obtained using different indicators and different comparison acids are to be expected from the probability of slight but unknown action between indicator and the acid radical. Nevertheless, assuming that conductivity measurements for uni-univalent acids give a true measure of degree of dissociation¹ we may conclude that the values we have presented for the hydrogen ion concentration in sulfuric acid are approximately correct.

A comparison of our values of hydrogen ion concentration with those recently presented in an article by Noyes and Stewart² will be of interest. Their method consisted in determining the relative concentrations of hydrochloric acid and sulfuric acid which drive back the ionization of picric acid to the same extent. Table IV gives values for the ratio of hydrogen ion concentration to the formal concentration of sulfuric acid, as obtained by the indicator method, and by the picric acid experiments of Noyes and Stewart.³ It has furthermore been shown by Noyes and Stewart by combining transference and conductivity data that certain limits can be calculated between which the hydrogen ion concentration must lie. These limits are also presented in the table. It will be noticed that none of the values for hydrogen ion concentration obtained by the picric acid method by Noyes and Stewart lie within the necessary limits

¹ For a consideration of the possibility that conductivity measurements do not give true values of the degree of dissociation, see an article by Tolman and Ferguson, *THIS JOURNAL*, 34, 232 (1912).

² *THIS JOURNAL*, 32, 1133 (1910).

³ The data of Noyes and Stewart presented in the table is that obtained using the value $\lambda_0 = 365$ for hydrogen ion.

which they have calculated. This probably means that the degree of dissociation of picric acid in the presence of the acids is not merely dependent on the concentration of hydrogen ion. Of the twelve different values obtained by the indicator method using different indicators and different comparison acids, only two lie outside the limits, and these are the only ones in which methyl green was used as an indicator. The general conclusion may be drawn that a comparison of the results obtained with a number of different acids and different indicators will lead for simple solutions to values of the hydrogen ion concentration of reasonable reliability.

Using the same method, a determination of the hydroxide ion concentration in solutions of di-acid bases is now being carried out by one of the authors (L. H. G.).

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI, OHIO, and ANN ARBOR, MICH.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF PLATINUM TETRAIODIDE AND OF IODINE IN ALCOHOL.

BY E. H. ARCHIBALD AND W. A. PATRICK.

Received February 12, 1912.

It is evident that the study of non-aqueous solutions must be greatly extended before the mystery surrounding the phenomenon of solution can be satisfactorily explained. Interesting examples of such solutions are those of the metallic iodides in ethyl alcohol. The following pages contain an account of some measurements of the electrical conductivity of solutions of platinum tetraiodide and of iodine in ethyl alcohol.

Materials Used.

Iodine.—Kahlbaum's resublimed iodine was ground with a little potassium iodide and again sublimed. This product, after being again carefully sublimed, gave the sample used in these experiments.

Platinum Tetraiodide.—Pure platinum was prepared by the repeated precipitation of ammonium chloroplatinate. From the pure platinum a solution of chloroplatinic acid was prepared and the platinum thrown down as the iodide with iodine and sodium iodide.

Ethyl Alcohol.—Kahlbaum's absolute alcohol was boiled for several hours with a large excess of pure calcium oxide and distilled. It was then allowed to stand for two days, with frequent shaking, over anhydrous copper sulfate. It was then distilled, reserving for the experiment only the middle portion of the distillate. This alcohol had a specific conductivity of 2.6×10^{-8} reciprocal ohms at 25°. If allowed to stand in contact with the air for only a few moments, its conductivity would increase tenfold.

Methyl Alcohol.—This alcohol was purified in the same way as the above, its specific conductivity was somewhat greater than that of the ethyl alcohol.

The conductivities of the above alcohols indicated that they were remarkably free from water. Every care was exercised to prevent the air of the laboratory from coming in contact with the pure solvents, or any of the solutions that would be appreciably affected thereby.

Apparatus Used.

The method of measuring conductivity was that of Kohlrausch. The bridge wire was carefully calibrated. Conductivity cells of the usual form were used, their constants being determined by means of 0.02 *N* potassium chloride. The temperature of the bath in which the electrolytic cells were kept was maintained at $25^{\circ} \pm 0.05$ by means of the usual regulator, the water in the bath being stirred by means of an electric motor. In the case of the measurements taken at 0° , the cells were placed in large felt-wound vessels which were filled with crushed ice.

The results obtained for the conductivity of the platinum iodide solutions in ethyl alcohol are shown in the following table. Under the term dilution are given the number of liters containing one equivalent or one-fourth of a gram-molecule of the iodide ($\frac{1}{4}\text{PtI}_4$). The conductivity values are expressed in reciprocal ohms and refer to a temperature of 25° :

SOLUTIONS OF PLATINUM IODIDE IN ETHYL ALCOHOL.

Dilution.	Specific conductivity.	Equivalent conductivity.
10.0	0.00145	14.5
20.0	0.000815	16.3
40.0	0.000450	18.12
80.0	0.000250	20.00
160.0	0.000137	21.90
320.0	0.0000735	23.5
640.0	0.0000384	24.6
1280.0	0.0000192	24.6

The conductivity is here large, compared with the conductivity of most substances in organic solvents being for instance considerably greater than the conductivity of alcoholic solutions of cadmium iodide, as measured by Jones and Carroll.¹ The conductivity of the most concentrated solution is a little greater than that of 0.01 *N* potassium chloride, and this notwithstanding the fact that the particles which carry the current are probably ions with relatively low migration velocities.

The equivalent conductivity increases with the dilution as is the case with almost all aqueous solutions, and it is particularly interesting to note that the equivalent conductivity becomes constant at great dilutions, which is the case with but few non-aqueous solutions. If we as-

¹ *Am. Chem. J.*, 32, 527 (1904).

sume that this constancy indicates that the dissociation is practically complete—a supposition we are continually making in the case of water solutions—and calculate the ionization coefficient for an 0.0125 *N* solution we find that at this concentration the platinum iodide is over 80% dissociated.

In connection with the above experiments we thought it would be of some interest to determine whether solutions of iodine in alcohol conducted the electric current; and if so, what the nature of this conduction is.

Few, if any, observations have been made of the conductivity of solutions of iodine in alcohols. Bruner¹ has measured the electrical conductivity of solutions of iodine in nitrobenzene and finds that the conductivity increases with time.

It is well known that when iodine is dissolved in organic solvents, the color of the solutions may be either violet or brown. In the case of the alcohols the color is brown. A great many investigators have concerned themselves with this variation in color. Paterno and Nasini,² from molecular weight determinations of iodine in benzene, concluded that in dilute solutions the iodine was present as I_2 , while in concentrated solutions the molecule varied between I_2 and I_3 . Loeb,³ from vapor tension measurements, found in the case of solutions of iodine in carbon disulphide, where the color is violet, a molecule varying from I_2 to I_3 , while the brown ether solutions gave I_4 as the formula.

Gauthier and Charpy⁴ considered that the difference in color was due to the formation of complex molecules. They laid stress upon the fact that brown solutions become violet when heated, while the violet solutions turn brown when cooled.

Beckmann,⁵ Hertz,⁶ and Nernst⁷ found experimental data that indicated I_2 as the formula for the iodine molecule in all solvents. Krüss and Thiele⁸ studied this question very thoroughly from various points of view. They came to the conclusion that the behavior of the iodine could be best explained by the difference in size of the iodine molecule; that is, by assuming that it existed as $(I_2)_n$ but behaved as I_2 as far as molecular weight determinations were concerned.

Lachman⁹ has shown that those solvents which give brown solutions

¹ *Bull. Acad. Sci., Cracow* (1907).

² *Ber.*, 21, 2153.

³ *Z. physik. Chem.*, 2, 606 (1888).

⁴ *Compt. rend.*, 110, 189.

⁵ *Z. physik. Chem.*, 5, 76 (1890).

⁶ *Ibid.*, 6, 385 (1890).

⁷ *Ibid.*, 6, 16 (1890).

⁸ *Z. anorg. Chem.*, 7, 52 (1894).

⁹ *THIS JOURNAL*, 25, 50 (1903).

of iodine are unsaturated, if the oxygen be regarded as tetravalent. On the other hand, the violet solutions are formed with such solvents as hydrocarbons which may be regarded as having their affinities satisfied.

Hillebrand and Glascock¹ have concluded from measurements of the lowering of the freezing point produced by iodine in various solvents, that in the case of the brown solutions there is a compound formed between the iodine and the solvent, while in the case of the violet solutions no such compound is formed.

If we assume, following Lachman, or Hillebrand and Glascock, that in the case of the brown solutions a compound is formed between the iodine and the solvent, we might expect from the behavior of solutions of alcohols in liquid hydrogen bromide that the compound would ionize to some extent and form a conducting solution. Again if, as suggested by Le Blanc, the iodine molecule breaks up into oppositely charged ions we would expect an appreciable conductivity.

Experimental.

Solutions of iodine in ethyl alcohol, 0.1 *N* and 0.01 *N*, were prepared and their conductivities measured. It was very soon apparent that the conductivity was increasing rapidly with the time. Accordingly, measurements were made at short intervals until the conductivity became constant. The time required for this to take place was about 25 hrs. at 25°. It was evident that a reaction was going on which involved the formation of a substance having a considerable conductivity in the alcohol.

0.1 <i>N</i> solution.			0.01 <i>N</i> solution.		
Time in hours.	Specific cond.		Time in hours.	Specific cond.	
0	4.39×10^{-5}		0	0.213×10^{-5}	
0.133	8.75	"	0.050	0.222	"
0.216	11.55	"	0.133	0.555	"
0.300	13.71	"	0.216	1.02	"
0.417	16.9	"	0.350	1.61	"
0.500	21.4	"	0.450	2.13	"
0.666	24.1	"	0.566	2.44	"
0.834	28.9	"	0.734	3.15	"
1.00	34.5	"	0.900	4.06	"
1.17	40.5	"	1.07	4.88	"
1.55	58.1	"	1.45	7.10	"
1.75	68.0	"	1.65	8.35	"
1.93	79.0	"	1.84	9.15	"
3.83	148.0	"	3.75	17.05	"
6.92	164.1	"	8.80	21.7	"
8.08	170.2	"	17.98	24.4	"
21.3	184.2	"	21.18	24.5	"
25.4	185.1	"	25.64	24.6	"

¹ THIS JOURNAL, 31, 26 (1909).

The values of the conductivity which show the rate at which the reaction was taking place in the case of the two solutions examined are given above. The conductivities are expressed in terms of reciprocal ohms.

The above values are shown graphically in Fig. 1, where the conductivities are plotted as ordinates, and time as abscissae. We notice that while in the case of the more concentrated solution the final value is much the greater, both attained their maximum value in about the same time.

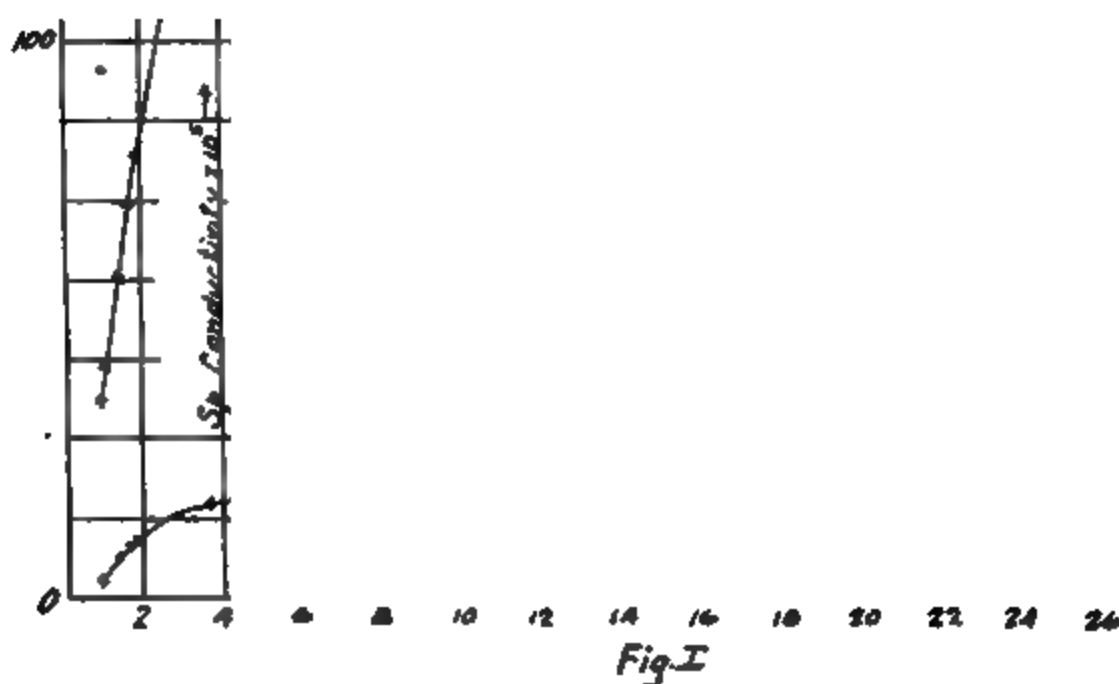


Fig. I

To ascertain whether this reaction was caused by the platinum black of the electrodes, two sets of solutions of the same concentration as those described above were made up. In one set a very small amount of platinum black was placed, but none in the other. After 25 hrs. the conductivities of all were measured, and those in which the platinum black had been had the same conductivity as the two solutions previously examined, while the set that had not been in contact with the platinum black had only very small conducting power, not much greater than what seems to be the initial conductivity of the iodine. Obviously the reaction had not taken place to any extent in the absence of the platinum black. Krüss and Thiele¹ have found that iodine reacts with alcohol at high tempera-

¹ *Loc. cit.*

tures. It may be that this is the same reaction, the velocity of which is increased enormously at low temperatures by the platinum black.

As might be expected as a result of this reaction, the color of the solution becomes much lighter.

The effect of temperature on the reaction was next examined. At 0° the conductivity of a newly prepared solution increased only very slowly with time, so slowly that at this temperature it was possible to carry out the measurements of the initial conductivity of the iodine. At -78° the conductivity did not change appreciably upon standing in contact with the platinum black for 45 minutes.

The following values were obtained by measuring the conductivity of the iodine in ethyl alcohol at 0° . The solutions were made up and measured as quickly as possible, the alcohol being cooled to 0° before introducing the iodine. The alcohol used was as pure as we could prepare. Following the usual procedure in the case of aqueous solutions, we have subtracted the conductivity of the pure alcohol from that of the solution in order to arrive more nearly at the conductivity of the iodine. We recognize, of course, that in the case of either type of solution, this is a questionable method of procedure.

Concentration of solution.	Specific conductivity.	Equivalent conductivity.
0.1 <i>N</i>	2.36×10^{-8}	0.0236
0.02 <i>N</i>	0.82 "	0.0413
0.01 <i>N</i>	0.67 "	0.0677

It is apparent from these measurements that the conductivity of the iodine in these solutions is very small. It may be asked if impurities present in either substance would not account for this observed increase in conductivity. In reply we can only say that each substance has been repeatedly treated in order to further purify it, and always gives the same conductivity.

It will be noted that the equivalent conductivity is increasing with the dilution, as is usually the case with aqueous solutions.

Measurements were also made of the conductivity of iodine in methyl alcohol. The measurements indicate a somewhat greater conductivity than in the case of the ethyl alcohol, with the same variation between the conductivity and the concentration, as shown above.

Bray has found the specific conductivity of aqueous solutions of iodine after they have stood for 15 minutes to be 3.8×10^{-6} which is of the same order, but a little greater than the above values.

A newly prepared solution of iodine in ethyl alcohol was tested as to its conductivity at 0° , then gradually cooled to -78° . Its conductivity continually decreased as the temperature fell, and no further indication could be found of a compound being formed even at this low temperature.

The conductivity of some very pure toluene was measured, and a solution of iodine prepared in this solvent, but not the slightest increase in conductivity due to the iodine present could be detected.

It seems not unlikely that the feeble conducting power of the alcoholic solutions of iodine, when first prepared, which are brown in color, is due to the dissociation of a compound formed between the alcohol and iodine. This compound is probably dissociated, however, only to a very small extent.

Summary.

(1) The conductivity of solutions of platinum tetraiodide in ethyl alcohol have been measured.

(2) The molecular conductivity of these solutions increases with the dilution and attains a constant value at dilutions of about 600 liters.

(3) The conductivity of solutions of iodine in alcohol increases with the time reaching a maximum value in about 25 hours.

(4) The velocity of the reaction which probably accounts for this increase in conductivity is greatly accelerated by the presence of platinum black.

(5) The initial specific conductivity of 0.1 *N* iodine in ethyl alcohol amounts to 2.4×10^{-6} reciprocal ohms.

(6) It is suggested that the brown color of the alcoholic solutions of iodine is due to the formation of a compound between the solvent and solute which is feebly ionized, giving the low initial conductivity observed.

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CONTRIBUTIONS TO THE ELECTROCHEMISTRY OF HYDRONITRIC ACID AND ITS SALTS. II. THE REDUCTION OF HYDRONITRIC ACID BY CUPROUS OXIDE.

BY J. W. TURRENTINE AND RAYMOND L. MOORE.

Received February 2, 1912.

In a previous communication¹ it was shown that corrosion efficiencies exceeding 100% were obtained when the metals magnesium, aluminium and zinc were made anode in a 2% sodium trinitride solution. In some instances the efficiencies approached 200%, the calculations being based on the cathode values obtained from a copper coulometer, and on the electrochemical equivalents of those metals computed from the valence normally displayed by them.

To account for the anomalously large values obtained under the conditions existing in these experiments, it was deemed plausible to hypothesize for those elements electrochemical equivalents twice as large as those ordinarily attributed to them. To do so it was necessary to consider them as dissolving electrochemically as metals of a lower valence. Thus,

¹ THIS JOURNAL, 33, 803 (1911).

electrochemical equivalents calculated for monovalent magnesium and zinc gave corrosion efficiencies which appeared to conform with Faraday's law, while those obtained for the same metals as divalent elements manifestly could not so conform. Other reactions into which these elements are known to enter make it necessary to hypothesize for them valences lower than that normally manifested by them.

Furthermore, in the experiments referred to, gaseous nitrogen was evolved at the anode in every instance, thus seemingly increasing the electrochemical efficiency.

In the stable compounds of magnesium and zinc, those elements exhibit only divalence, from which it may be concluded that compounds in which they exhibit monovalence are sufficiently unstable to make their isolation difficult, or impossible. So, such compounds, forming at an anode undergoing corrosion, must break down practically instantaneously to the more stable form. The change of the metal from the monovalent to the divalent form is an oxidation and therefore involves a reduction of the oxidizing agent.

In a previous research¹ the same explanation was advanced for a similar anomalous behavior of magnesium and aluminium anodes. In substantiation of the explanation, an evolution of hydrogen at the anode was observed. This was taken to be a product of the reaction between the unstable metallic compounds and water—being a reduction of water.

In the study of the electrochemical corrosion of metals in sodium trinitride solution, the gas evolved at the anode was nitrogen, with, perhaps, in some cases, a small proportion of hydrogen. Nitrogen, normally, would be evolved at the anode in such a solution, resulting from the discharge of the nitride ions, if the corrosion were not quantitative.² However, even then, in instances, the equivalent in nitrogen of the corrosion deficiency was exceeded. Clearly, the indication was that some nitrogen was being liberated through a secondary, anode reaction; and, as hydrogen was not evolved, it appeared that the oxidation was being effected by some substance capable of yielding nitrogen as a reduction product. Such a substance was the sodium trinitride, or the nitride ion.

The reduction of hydronitric acid has been shown to yield ammonia under certain conditions.³ A reaction was proposed, therefore, which considered the formation of ammonia as well as the evolution of nitrogen. This reaction may be represented by the equation:



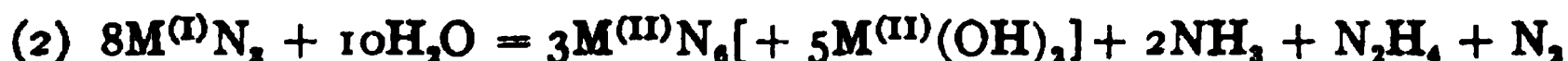
In substantiation of the proposed reaction, the evolution of nitrogen having been determined, the solution which had been undergoing elec-

¹ "Reversed Electrolysis," *J. physic. Chem.*, 12, 448 (1908).

² Szarvasy, *J. Chem. Soc.*, 77, 603 (1900).

³ Cf. reference to literature, *THIS JOURNAL*, *loc. cit.*

trolysis (with zinc anode) was analyzed for ammonia, with affirmative results. Furthermore, in the solution in which magnesium anodes were corroded, hydrazine also appeared to be present, in addition to ammonia. To account for the additional reduction product, the following equation was proposed:



Such reactions as these should lend themselves to experimental verification. While it may not be possible to prepare at will magnesian, aluminous, or zincous compounds, and to permit them to react with hydronitric acid, it should be possible to induce reactions, in a general way similar to those proposed, with metallic compounds, more stable than the hypothetical magnesium and zinc compounds, but still easily oxidized.

It was deemed possible that cuprous compounds might be induced to react with hydronitric acid in a manner analogous, if not similar, to that hypothesized for magnesian, zincous and aluminous compounds. However, it was recognized that the former should be a weaker reducing agent than the latter, judging by their relative positions in the electrochemical series; and that, if the liberation of the so-called nascent hydrogen functioned in the reduction by the latter, the cuprous compound could not effect the desired reduction of the hydronitrogen.

The reactions, then, between a cuprous compound and hydronitric acid, or the trinitride ion, should result in either the precipitation of a mixture of metallic copper and cupric trinitride,¹ a reaction analogous to that of sulfuric acid with cuprous oxide in the cold, or in the oxidation of the copper to the cupric condition with the formation of ammonia, or of ammonia and hydrazine, within the solution, and with the evolution of gaseous nitrogen. The demonstration of the occurrence of such a reaction with cuprous compounds and hydronitric acid, it was believed, would be acceptable as a sort of proof of the correctness of the proposition that reactions of the same type occur at magnesium and zinc anodes in trinitride solutions.

To reproduce chemically, then, or to analogize, the hypothetical reactions induced electrochemically, the experiments to be described in the following paragraphs were performed:

Historical.—Curtius and Rissom² prepared compounds of copper with hydronitric acid by treating (1) copper sulfate with sodium trinitride, in aqueous solution, and (2) by allowing an aqueous hydronitric acid solution to react with metallic copper. In both cases, brown-yellow, crystalline salts were obtained, difficultly soluble in water, the one prepared

¹ Cupric trinitride is a sparingly soluble body. Cf. Curtius and Rissom, *J. prakt. Chem.*, 58, 261 (1898).

² *Loc. cit.*

from copper sulfate showing the composition corresponding to the formula CuN_6 . While, superficially, both substances were identical, the authors having in mind the analogy which appeared to exist between hydronitric acid and the halogen hydracids, expected to obtain a cuprous compound from the interaction of metallic copper and hydronitric acid, corresponding to cuprous chloride, obtainable from the interaction of metallic copper and hydrochloric acid. In a later communication,¹ Curtius mentions the existence of cuprous trinitride, obtainable by treating cuprous oxide with hydronitric acid. This compound was described as deep red in color.

Dennis and Isham² prepared cupric-ammonium trinitride ($\text{CuN}_6 \cdot 2\text{NH}_3$) and cupric-pyridine trinitride ($\text{CuN}_6 \cdot 2\text{C}_5\text{H}_5\text{N}$), crystalline compounds.

In the corrosion of copper anodes in sodium trinitride solution, copious precipitates, yellow in color, were obtained.³ This was taken to indicate that copper was dissolving from the anode in the cuprous condition and was being precipitated subsequently as cuprous hydroxide by interaction with sodium hydroxide from the cathode region.

Experimental.

Preparation of Material.—Hydronitric acid was prepared by the distillation of a solution of sodium trinitride (commercial), obtained from Raschig, acidified with sulfuric acid. The distillate was diluted to an approximately 2% concentration.

Cuprous oxide was precipitated by glucose from an alkaline double tartrate solution. This was washed repeatedly with distilled water. Other portions were prepared by electrolyzing a cold solution of sodium chloride between copper electrodes.

The Interaction of Hydronitric Acid and Cuprous Oxide.—On the addition of hydronitric acid to yellow cuprous oxide, the latter quickly changed from the granular to a flocculent condition, becoming much more bulky. Its color changed simultaneously from the reddish yellow of the cuprous oxide to a brown yellow.⁴ The precipitate reacted with concentrated hydrochloric acid, yielding a white solid, presumably cuprous chloride. With concentrated sulfuric acid, a precipitate of dark red, metallic cop-

¹ *Ber.*, 23, 3023.

² *THIS JOURNAL*, 29, 18 (1907).

³ *Ibid.*, 33, 803 (1911), see p. 824.

⁴ The color of the precipitate as first formed appears to be a function of the color of the cuprous oxide used. If that be yellow, the color of the precipitate obtained with hydronitric acid is more yellow; if the color be red, the precipitate obtained is at first red. This fact probably accounts for Curtius' statement (*Ber.*, 23, 3023) that cuprous trinitride is red. As the transformation from cuprous oxide to the nitrogen compound is, of course, not an instantaneous one—one of the reacting substances being a solid—the first colors obtained are composite of those of the oxide and the nitrogen compounds resulting. In the light, the color of the cupric trinitride eventually prevails and the substances become dark brown.

per resulted. These reactions are characteristic of cuprous compounds and show the presence within the precipitate of some cuprous compound. The compound was soluble in ammonium hydroxide and ammonium chloride solutions. In the latter a colorless solution resulted, turning blue in contact with the air. The solid, on exposure to air, rapidly became dark brown and on drying was extremely explosive (CuN_3 ?); on standing in a test tube, covered with its mother liquor, but exposed to diffused sunlight, its color changed from yellow to the dark brown of cupric trinitride. The darkening in color occurred earlier, and was more intense on the side toward the source of light. This change was accompanied by a slow *evolution of gas*. The supernatant liquid was straw-yellow in color,¹ from which, by the very careful addition of dilute ammonium hydroxide, with heating, there was produced a slight yellow precipitate, soluble in a slight excess of the precipitant. This was taken to be cuprous hydroxide. To other portions of the supernatant liquid was added potassium hydroxide. On warming, *ammonia was evolved*, as was attested both by litmus paper and the sense of smell. Tests for hydrazine with Fehling's solution, applied to the supernatant liquid, gave negative results.

The presence of sulfuric acid (5 cc. 6 *N* to 10 cc. 2% HN_3 soln.) retarded the color changes; however, the effervescence produced by the reaction between the cuprous oxide and hydronitric acid was more marked in its presence, and the production of ammonia was quite as marked. Dilute sulfuric acid added to the solid after it had become black from exposure to the light restored the original pale yellow color, the superficial coating of dark brown solid dissolving in the acid to a blue solution.

While in every instance where the precipitate was exposed to the light it turned dark brown, when kept in the dark it became white and remained so seemingly indefinitely. Its supernatant liquid, acidified with hydronitric and sulfuric acids, gradually assumed the blue color of the cupric ion.

Small portions of the white precipitate were exposed to the focused light of a carbon arc (15 amp., 110 volt) for various lengths of time, an exposure of 5 sec. being sufficient to turn the solid a dark brown. At the same time there was a marked evolution of gas. The coloration was only superficial, the dark color on the surface protecting the colorless compound beneath. This became evident on stirring.

In order to determine the nature of the gas evolved, a portion of the cuprous oxide, in a 15 cc. test tube, was treated with 10 cc. hydronitric acid solution and 5 cc. 6 *N* sulfuric acid.² The tube was closed with a

¹ THIS JOURNAL, 33, 803 (1911), see p. 824.

² The sulfuric acid was added because in its presence, it has been noted, the effervescence is more rapid. The presence of the acid, however, is not essential to the effervescence.

one-holed rubber stopper through which was inserted a capillary delivery tube. This was bent at the proper angles so as to deliver the gas into an inverted buret, filled with water, to serve as a gas holder. The test tube was so filled that when the stopper was forced into position all of the gas and some of the liquid were forced out through the capillary. Thereafter, any gas delivered into the gas holder was only that evolved from the reacting substances within the tube.

At the end of about one week 14 cc. of gas had been collected. This was analyzed in separate portions for oxygen and hydrogen, respectively, by shaking with alkaline pyrogallol in a Hempel pipet and by passing over freshly ignited palladium black, at a temperature near 100°. The first portion of 5.8 cc. was mixed with 12.6 cc. of pure nitrogen,¹ making a total volume of 18.4 cc. The volume remaining after the absorption in alkaline pyrogallol and palladium black was 18.2 cc., showing a contraction of 0.2 cc. The second portion, 8.8 cc., was added to the residues from the preceding analysis, making a total volume of 27.0 cc. The residue from the palladium absorption measured 26.8 cc. showing an absorption of only 0.2 cc., a value hardly outside the limits of experimental error. On the basis of these analyses (and on others of volumes of gas obtained under like conditions from other compounds reacting with hydronitric acid) the gas evolved under these experimental conditions was taken to be practically pure nitrogen.²

The foregoing observations indicate that cuprous oxide reacts with hydronitric acid to form an unstable compound containing nitrogen which, in contact with an excess of the acid, undergoes gradual transformation into cupric trinitride. The transformation, being an oxidation, results in the reduction of the oxidizing agent, hydronitric acid, and yields, as the reduction products of that acid, ammonia and nitrogen.

The following equation is proposed to represent qualitatively the reduction of hydronitric acid by cuprous oxide:



They indicate further that this transformation takes place more readily in the presence of sulfuric acid, a fact which would be explicable on the supposition that the protective coating of cupric trinitride, difficultly soluble in water, is constantly being removed by solution in sulfuric acid.

There is evidence also that the oxidation of cuprous trinitride by hydronitric acid is a reaction that is greatly accelerated by light.

Analysis. — Numerous attempts were made to determine quantita-

¹ From previous analyses; added to secure a convenient volume.

² The activity of the palladium black was repeatedly tested with volumes of hydrogen prepared from zinc and sulfuric acid; the hydrogen was invariably absorbed quantitatively.

tively the copper and nitrogen content of the compound produced from cuprous oxide. On account of its lack of stability in the air and light, portions were prepared and were filtered, washed and dried in an atmosphere of hydrogen, the entire operation being carried out in red light, or in the dark. Because of its supposed explosive character, it was filtered in small amounts on separate filters. To this purpose a Bruehl receiver for use in vacuum distillations was adapted. The rack for holding the receiving tubes was supported on a single glass foot and was held upright by wedges. In it were placed five funnels containing tared filter papers. The side apertures were provided with rubber stoppers through which were inserted glass tubes for the entrance and exit of a stream of hydrogen. The tube in the lower side aperture was so bent as to enter a slight depression in the lowest part of a sloping false bottom of paraffin, and was provided at its inner end with a short section of rubber tubing to make a closer contact with the bottom of the depression. Thus all liquids coming from the various filters were made to flow into the depression and were forced thence out through the exit tube. In this way the last drop of liquid could be blown out by the issuing stream of hydrogen. The stem of a dropping funnel entered through the opening in the lid. It was bent at an angle and could be turned so as to deliver solutions and suspended precipitates into the various filters as desired. Wash liquids were admitted in a similar manner.

The air was displaced in the filtration vessel by hydrogen. Portions of the yellow substance prepared and filtered in the manner indicated were washed with distilled water, absolute alcohol and ether, previously freed from air by shaking with, and maintaining under hydrogen. They were then dried for 48 hours by passing a stream of hydrogen, dried over concentrated sulfuric acid, through the apparatus. After the washing, the vessel was enveloped in black paper to exclude light. The precipitates, together with the papers holding them, were then weighed between tared watch-glasses. It was noted that they lost weight rapidly on the balance pan. They were transferred to graduated flasks containing ammonium hydroxide; after they had dissolved, the flasks were filled to the mark with water.

For the determination of hydronitric acid, aliquot portions were transferred rapidly to distilling flasks containing sulfuric acid in excess over that requisite to the neutralization of the ammonium hydroxide and were distilled in the usual way into receiving solutions of silver acetate.

Copper was determined electrochemically from the solution remaining in the distilling flask after the distillation.

Strictly concordant results were obtained for both nitrogen and copper; these were found to be present in approximately equivalent amounts, with copper in slight excess; of nitrogen there was found 29.6 % and of

copper 49.1%, equaling 78.7%. If water of combination be considered as making up the balance, these values are in close agreement with the formula $\text{CuN}_3 \cdot 2\text{H}_2\text{O}$.

From a sample representing 0.0348 g. material was obtained 0.0368 g. AgN_3 , equivalent to 0.0103 g. N_3 (= 29.6%). This weight of nitrogen, on the basis of the formula $\text{CuN}_3 \cdot 2\text{H}_2\text{O}$, is equivalent to 0.0156 g. copper, (found, 0.0167 g. copper) and to 0.0088 g. water; total, 0.0347 g.

Under the conditions existing in these experiments, one would expect to obtain cuprous trinitride. In the absence of a determination of water, it cannot be said with definiteness whether the formula proposed represents the actual composition of the compound, or is in agreement with the values obtained only through a coincidence.

The excess in copper over nitrogen, it may be pointed out, is to be expected when it is remembered that a reaction between a solid and a liquid may quite easily be incomplete, due to the protective coating on the solid of the product of the reaction, where the product is likewise a solid. It is to be expected, then, that a small amount of cuprous oxide would still be present.

The application of the results described in the foregoing paragraphs to the anomalous electrochemical corrosion of magnesium and zinc in sodium trinitride solution has been made, through predicted analogies, in the preamble. They tend to support, furthermore, the interpretation of the phenomena observed when copper is made anode in that solution. The formation of the highly explosive black compound on the anode may be explained as the result of the nitridation of the soluble cuprous trinitride to the insoluble cupric compound.

Summary.

In the reaction between hydronitric acid and cuprous oxide the acid plays the role of an oxidizing agent and is reduced to ammonia and nitrogen.

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THE ACTION OF HYDRONITRIC ACID ON CUPROUS CHLORIDE AND METALLIC COPPER.

BY J. W. TURRENTINE AND RAYMOND L. MOORE.

Received February 2, 1912.

Cuprous Chloride.—When cuprous chloride is treated with dilute hydronitric acid it is transformed from the white, crystalline form into a bulky, yellow and flocculent condition. When the latter substance is treated with hydrochloric acid, the white crystalline condition is resumed, a fact which indicates that the reaction is reversible.

Cuprous chloride, prepared by one of the well known methods, was washed by decantation with distilled water until yellow tints began to

appear. It was then treated with a 2% solution of hydronitric acid. When treated with a single portion of the acid a compound resulted which was fairly stable in the air and light, and which contained both chlorine and nitrogen. This was filtered, washed and dried without any great change in color. Portions of the dried substance dropped upon a hot plate exploded with a sharp report and a flash of green flame. When it was blown into a flame, beautiful green scintillations were produced.

A small portion of this substance was prepared for analysis in the same way as was the cuprous trinitride, as described in the foregoing paper. The results of the analyses were concordant and showed the presence in the mixture of 53.7% copper and 11.2% chlorine. As the substance must be regarded as a mixture, no importance can be attached to the analytical data.

When the cuprous chloride was treated repeatedly with fresh portions of hydronitric acid solution, a substance was formed which was quite sensitive to light and air, and resembled closely the product obtained from the interaction of cuprous oxide and hydronitric acid. A microchemical analysis of this material showed the presence of the trinitride, and the absence of the chloride ion, from which it must be concluded that the compound was the cuprous trinitride.

Small portions of the substance containing both chlorine and nitrogen, together with the solutions in which they had been formed, were left undisturbed for several weeks in test tubes closed with corks. Brilliant, black crystals, resembling jet, formed in the supernatant solution and grew radially, while the original solid slowly disappeared. The mother-liquor was green in color. Under the microscope the jet-like crystals were found to be bundles of closely packed, translucent needles, of a dark, brownish green color. A microchemical analysis showed the presence of the trinitride ion and the absence of the chloride ion—a white precipitate was produced when the vapor from the nitric acid solution of the substance came into contact with silver nitrate solution; this precipitate was soluble in nitric acid, and the addition of silver nitrate to the solution from which the vapor was evolved gave no precipitation.

Minute pieces of the needles dropped upon a hot plate exploded with a sharp snap and a flash of green flame. The compound was taken to be crystalline cupric trinitride, resulting from the gradual formation of cupric ions in the presence of the trinitride ions. Cupric trinitride has been shown to be a substance but sparingly soluble in water.¹ However, because of its explosive nature, the compound was not submitted to a quantitative analysis.

Metallic Copper.—Finely divided metallic copper was prepared from copper sulfate by precipitation with granulated zinc. On the complete

¹ Curtius and Rissom, *J. prakt. Chem.*, 58, 261 (1898).

precipitation of the copper, the precipitate was boiled with successive, fresh portions of dilute sulfuric acid until there was no further evolution of gas. This procedure should have insured the complete removal of all zinc.

Metallic copper, prepared as stated, was treated with a few cubic centimeters of 2% hydronitric acid. A slow evolution of gas immediately ensued. The red color of the copper gradually changed to the dark brown of the flocculent cupric trinitride. The supernatant liquid became neutral to litmus and, after about a week, deposited pale blue copper compounds, presumably basic. The addition of a drop of sodium hydroxide to the solution produced a yellow precipitate, doubtless of cuprous oxide. *Ammonia*, was evolved without warming and in such amounts as to be distinctly evident to the sense of smell. Its evolution was further attested by the bluing of red litmus paper and the blackening of mercurous nitrate paper. Tests for hydrazine with Fehling's solution showed no reduction.

In order to determine the composition of the gas evolved from the action of hydronitric acid on copper, the reaction was allowed to take place in a stoppered tube and the evolved gas was conducted into a gas-holder, as described in the account of the corresponding experiment with cuprous oxide.

In twelve hours 25 cc. of gas had accumulated. This was analyzed in portions, the following values from a single analysis being typical: A sample, 17.0 cc. in volume, was added to a volume of 33.2 cc. of pure nitrogen,¹ making a total volume of 50.2 cc. Over alkaline pyrogallol there was a contraction to 49.7 cc., representing a loss in volume of 0.5 cc. Passing the gas repeatedly over palladium black, at a temperature near 100°, caused no further contraction; accordingly, it was taken to be *nitrogen*. *Ammonia* was found to be present in the solution resulting.

These experiments, although extremely simple, establish the fact that the reduction of hydronitric acid by metallic copper yields ammonia and nitrogen as reduction products. Copper dissolves in hydronitric acid with an effervescence of nitrogen. The ammonia resulting from the reaction neutralizes its equivalent of hydronitric acid to form ammonium trinitride. It was assumed, without analysis, that the copper became, superficially at least, the cupric trinitride.² The following equation is proposed to represent the reaction between copper and hydronitric acid:



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¹ From a previous analysis. The addition was merely to give a convenient volume with which to work.

² THIS JOURNAL, 33, 803 (1911), see p. 824.

THE REDUCTION OF HYDRONITRIC ACID. I. A PRELIMINARY NOTE ON THE STRUCTURE OF HYDRONITRIC ACID.

BY J. W. TURRENTINE.

Received February 12, 1912.

Following experiments by E. Fischer,¹ which, in the light of our fuller knowledge of the behavior of hydrazine upon oxidation, could at least

be given a different interpretation—the structural formula, $\text{H}-\text{N} \begin{array}{l} \nearrow \text{N} \\ \parallel \\ \searrow \text{N} \end{array}$,

has been given to hydronitric acid; this formula has no parallel among the other nitrogen compounds or inorganic acids, and places that acid structurally in a quite isolated position.

Heretofore, hydronitric acid has been regarded as an analog of the halogen hydracids, and it is possible to construct a sort of analogy between them. It may be observed, however, that this analogy is based almost entirely on solubilities and not on reactions.²

In a study of the reduction of hydronitric acid, it was found that many metals below magnesium in the electrochemical series, when acted upon by hydronitric acid, led to the formation of ammonia and free nitrogen as reduction products (Equation 1). No hydrogen was evolved. In one instance hydrazine appeared as an additional reduction product.

In the reduction of the acid by oxidizable metallic compounds, the action resulted in a compound of the metal in which the latter possessed a higher valence, and in ammonia and nitrogen as the reduction products of the acid (Equation 3).

With certain oxidizable, non-metallic compounds the acid was reduced with the formation of ammonia and nitrogen, again, as the reduction products, and with the negative element of the reducing agent appearing in a higher state of oxidation (Equation 5).

Certain metals lying near the bottom of the electrochemical series do not displace the hydrogen of acids because of the large difference between the electrode potentials of those metals and hydrogen. The reaction may be regarded as a reversible one, the reverse action taking place at a much greater rate than the direct one. A substance able to reduce the active mass of the hydrogen—a depolarizer—prevents the reverse action and enables the direct action to take place to completion.

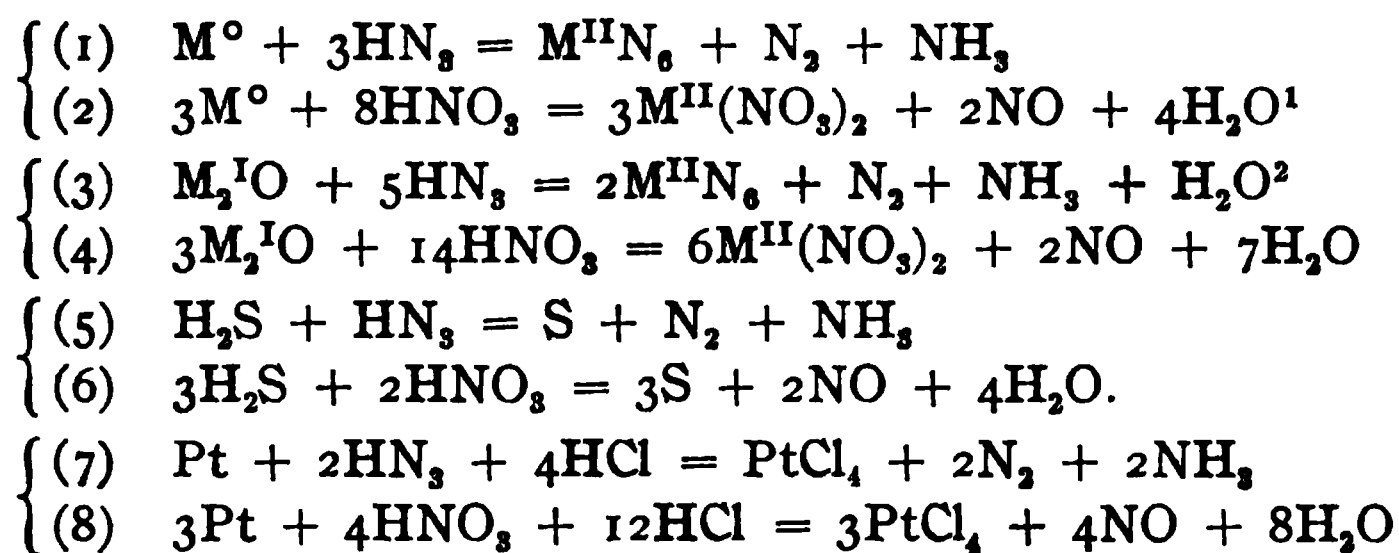
Hydronitric acid was found to be an efficient depolarizer. In its presence hydrochloric acid dissolved platinum. Ammonia and nitrogen were among the reduction products (Equation 7).

When we consider the behavior of hydronitric acid in the reactions mentioned and attempt to bring it into line with that of other inorganic acids under like conditions, we are struck at once with the parallelism

¹ "Ueber die Hydrazinverbindungen," *Ann.*, 190, 67 (1878), see p. 92.

² THIS JOURNAL, 33, 803 (1911).

between the chemical properties of this acid and those of nitric acid. This analogy is brought out when we examine the equations representing the reactions of the two acids with the respective reducing agents, as follows:



An inspection of the first two equations brings out the following points: In neither reaction is hydrogen evolved. In both cases a portion of the acid radicle appears as a gaseous product, in one instance consisting chemically of a nitrogen atom united to a nitrogen atom, and in the other, a nitrogen atom united to an oxygen atom. In the one case ammonia results, and in the other, the strictly analogous substance, water, is produced. That the same analogy holds throughout the series of equations is perfectly evident.

Assuming that an analogous reaction implies an analogous structure, the formula $H-N=N\equiv N$ is proposed for hydronitric acid, which is a parallel formula to $H-O-N \begin{smallmatrix} =O \\ =O \end{smallmatrix}$, commonly accepted as representing the structure of nitric acid. In the one instance a pentavalent nitrogen, the nucleus of the molecule, is united to nitrogen, and in the other, to oxygen.

When we review the structure of the inorganic acids, such as cyanic, thiocyanic, nitrous, etc., we see that the various positions in the molecules are occupied in turn by the negative atoms to form the various acids. In hydronitric acid all the positions are occupied by nitrogens. Furthermore, the hydroxyl group of nitric acid is replaced in hydronitric acid by the analogous imide group.

Hydronitric acid, then, must be regarded as a nitridizing agent, analogous to nitric acid, an oxidizing agent; and just as nitric acid is a hydrated oxide of nitrogen, hydronitric acid may come to be regarded as an ammoniated nitride of nitrogen.

These conclusions are supported by and are derivable from numerous

¹ While it is recognized that other products may, and do, result from the action of nitric acid on metals, those represented above are regarded as the most typical.

² Two reactions are represented by this equation, one the action of an acid on an oxide to form a salt and water, and the other the nitridation of the metal to a higher valence.

other considerations to be presented subsequently. In a recent article Thiele¹ has assigned hydronitric acid the same structure as that advanced in this note. While the conclusions are similar, the one was arrived at through organic considerations, while the other was reached through a study of the inorganic chemistry of the acid. That the conclusions were arrived at quite independently may be further attested by the fact that the matter here presented was communicated by correspondence, and otherwise, to various members of the chemical profession almost a year ago, and months before the appearance of the article in the *Berichte*.

WESLEYAN UNIVERSITY.

SOLUBILITY OF WROUGHT TUNGSTEN AND MOLYBDENUM.

BY W. E. RUDER.

Received February 5, 1912.

Since the production of tungsten and molybdenum metals in a malleable and ductile form,² various interesting applications have been found for these metals. Probably the most extensive use for tungsten at present is in metal filament lamps, but this metal, combining the physical properties of high melting point (3000°), high specific gravity (19.3), low vapor pressure and high heat conductivity, has found use as a contact metal in numerous current interrupting devices, as a target in Röntgen tubes, and as a possible projectile material.³

It is the purpose of this paper to point out some of the chemical properties of these wrought metals, which, combined with their physical properties already described, may broaden the field of application of these two interesting metals.

Tungsten.

In the following experiments the samples of metal used were all of the same surface and shape. They were discs, of sheet tungsten, such as are now being used for X-ray targets, and are 18 mm. in diameter and about 2.5 mm. thick. The surface area was $510 + 140 = 650$ sq. mm. on the average. The weight, according to thickness, varied from 9 to 12 grams.

Solubility in Hydrochloric Acid.—Wrought tungsten is insoluble in hydrochloric acid of any concentration at room temperature and only very slightly so at 110° . After 45 hours the hot, concentrated acid (sp. gr. 1.15) showed no effect upon the tungsten. After 175 hours, however, a black coating of oxide formed and the metal lost 0.5% in weight.

In dilute acid, at 110° , it lost 0.05% after 22 hours but showed no further loss after 50 hours. After 175 hours the metal was coated with tungstic oxide and there was a gain in weight of 1% due to oxidation. This

¹ *Ber.*, 44, 2522 (1911).

² Fink, *Trans. Am. Electrochem. Soc.*, 17, 229-234. Coolidge, *Proc. Am. Inst. E. E.*, 29, Part II, 961-965.

³ Coolidge, *J. Ind. Eng. Chem.*, 4, 2 (1912).

oxide formed an adherent coating and protected the metal against further loss.

Solubility in Sulfuric Acid.—At room temperature this acid has no effect upon wrought tungsten nor has the dilute acid at 110° . Concentrated acid attacks it very slowly at 110° , the loss in weight being 0.1% after 18 hours, 0.16% after 40 hours, and 0.63% after 175 hours. Increased temperature hastens the action, for at 200° 0.62% was lost in four hours. In another experiment 1.18% dissolved in 8 hours.

Solubility in Nitric Acid.—Concentrated nitric acid at 110° showed no action on tungsten after 48 hours other than a slight dulling of the bright, metallic surface. The dilute acid, however, produces the yellow oxide on the surface. There is a slight gain in weight after 15 hours and then no further change even after 175 hours' immersion.

Solubility in Aqua regia.—Aqua regia, at room temperatures, oxidizes the surface to tungstic oxide. After 215 hours the loss in weight was 0.31%. At 110° the chlorine was all driven off in about 4 hours and the tungsten disc had lost 0.1% and it was covered by a tough, greenish yellow deposit. If this coating of oxide was allowed to remain, continued boiling in fresh aqua regia had no further effect upon the metal.

Solubility in Hydrofluoric Acid.—This acid, hot or cold, did not attack tungsten, not even to the extent of dulling its polished surface, during numerous evaporations of the acid.

Solubility in Potassium Hydroxide.—Potassium hydroxide solution, of any concentration, does not attack wrought tungsten but the fused alkali attacks the metal slowly. In this case there was 31% loss in weight after 15 hours and in about 40 hours the disc had all dissolved.

Solubility in Alkaline Carbonate.—In fused sodium carbonate, potassium carbonate, or mixtures of the two, tungsten dissolves slowly. About 2.5% loss was noted in four hours. The addition of potassium nitrate hastens the solution considerably. In this experiment 32% dissolved in six hours.

Other Experiments.—A saturated sodium hypochlorite solution was found to attack tungsten at the rate of 4.27% in twenty hours. A mixture of sulfuric acid and chromic anhydride did not act upon the metal. A mixture of hydrofluoric and nitric acids dissolves tungsten very rapidly with the evolution of nitric oxide and the production of tungstic oxide.

Molybdenum.

In the following experiments small strips of sheet molybdenum were used. These were $30 \times 9 \times 0.4$ mm., having a total surface of 540 sq. mm.

Hydrochloric acid, diluted, slowly dissolves molybdenum at 110° to a brown solution with the formation of some black oxide, probably Mo_2O_3 . The loss in weight was 20.3% after 18 hours. The more concentrated acid (1.15) has a much slower action. After keeping the metal for 18

hours in this acid at 110° C. the total loss of metal was only 0.34% and the surface was still bright.

Sulfuric acid, diluted (sp. gr. 1.30), at 110° does not attack molybdenum. The concentrated acid (sp. gr. 1.82) attacks it but very slowly at this temperature. Only 0.29% loss in weight was found after 18 hours. With elevated temperatures, however ($200-250^{\circ}$), the metal dissolves rapidly to a green solution, with the evolution of sulfur dioxide.

Nitric acid, concentrated (sp. gr. 1.40), dissolves molybdenum slowly with the formation of molybdic anhydride, MoO_3 , which deposits on the surface of the metal and retards the action. The more dilute acid (sp. gr. 1.15), however, attacks the metal rapidly.

Aqua regia also dissolves the metal rapidly, especially if heated.

Hydrofluoric acid (hot or cold) does not attack molybdenum.

Potassium hydroxide solutions do not attack molybdenum, but it is soluble in the fused alkali.

It will be noted that both of these metals are to a certain extent acid-resisting and this is due principally to the formation of an acid-resisting coating of oxide. Tungsten is attacked most rapidly by fuming sulfuric acid, and this only to the extent of 1.2% in 8 hours.

Molybdenum is much more easily dissolved than tungsten. It resists concentrated hydrochloric and sulfuric acids at moderate temperatures (below 125°) fairly well and is untouched by hydrofluoric acid.

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PERCHLORIC ACID IN ELECTROCHEMICAL ANALYSIS.

BY W. S. HENDRISON.

Received January 17, 1912.

In the latter part of the academic year 1910-'11 the writer made electrolytic separations of certain metals from perchloric acid solution with good results. The pressure of other duties made it necessary to discontinue the work for a time. In the meantime Henryk Golblum¹ has published a paper on the determination of perchloric acid in the perchlorates of nickel and cobalt, his method being to deposit the metals electrolytically and titrate the acid left in solution. Though the determination of the metals was apparently not his object, he states that they were deposited quantitatively, and that the method for the determination of the acid would probably be found applicable in all perchlorates whose metals can be deposited in weak acid solutions. Since these statements seem to foreshadow work in the direction of my own, it seems desirable to publish a brief statement of the work done in this laboratory.

¹ *Z. anal. Chem.*, 1911, 741.

Several years ago, while studying the action of certain oxidizing acids on metals, the writer became much impressed with the great indifference of perchloric acid in solution toward chemical reagents and especially those of a reducing character. The only reducing agents that are effective seem to be freshly precipitated ferrous oxide, sodium thiosulfate and to a small extent some oxides of nitrogen. Certain other substances decompose it when highly heated with it in sealed tubes. There seems to be no other strong, that is highly dissociated, oxygen holding acid comparable with perchloric acid in the indifference of its negative ion toward such agents, save sulfuric acid, and even this is reduced by hydriodic acid and many other agents that under like circumstances are ineffective toward perchloric acid. In short, in water solution perchloric acid exhibits only the properties due to its primary ions, and there are no side reactions due to the decomposition of its negative ion.

It seems that such a stable and strong acid should find more uses, interesting to the chemist, at least, and possibly of practical importance if cheaper methods could be found for its manufacture. Since the choice of solvents is somewhat restricted in electro-chemical analysis, it occurred to the author that the question of the availability of perchloric acid in this capacity was worthy of study. As anticipated, it was soon found that some metals may be easily and completely deposited in weighable form from perchloric acid solutions; moreover, since the acid is so strong and stable, metals may easily be converted into perchlorates for electrolysis.

Perchloric acid readily dissolves many oxides of the heavy metals. Oxides, metals, or other refractory substances, may also be converted into nitrates with nitric acid, and this acid replaced by evaporation with an excess of perchloric acid. To test this point a known volume of a standard potassium nitrate solution was evaporated on the water bath with an excess of perchloric acid. Water was added and the evaporation was repeated, after which a determination showed that 94% of the combined nitric acid had been replaced. In parallel experiments equal weights of copper were dissolved in nitric acid, and evaporated, one with and the other without the addition of an excess of perchloric acid. Determination of the nitric acid in the residues showed that 98% had been expelled by the perchloric acid. There is no danger of decomposing perchloric acid by evaporation on the water bath, and it is probable that considerably higher temperatures may be used.

To the present time electrolytic determinations of three metals have been made from perchloric acid solution: copper, silver and cadmium.

Copper.

Copper oxide was prepared from pure copper sulfate. After thorough washing it was dried and heated for an hour in a porcelain boat

in a current of oxygen. Small portions were weighed in a platinum dish and dissolved in a small excess of pure perchloric acid. The acid showed scarcely a trace of hydrochloric, chloric acid or any other impurity. The solution was made up to 100 cc. with pure water and subjected to the electric current for about three hours. The revolving anode was used. At the beginning the current showed 0.2 ampere to one square decimeter of cathode surface and 2.5 volts; later the current was increased. At the end of each experiment the solution was siphoned off and replaced with water while the current was running, and the free perchloric acid was titrated. Two analyses are as follows:

	Copper oxide.	Calculated copper.	Copper found.	Acidity.
1.....	0.3011	0.2405	0.2407	0.1 N
2.....	0.3341	0.2669	0.2665	0.09 N

To test the method further, copper was deposited from pure copper sulfate. This was dissolved in nitric acid and the acid was expelled by evaporation with an excess of perchloric acid, using the platinum dish in which the metal was deposited. The metal was then redeposited, washed, dried and weighed. This process was repeated three times with the same portion of copper, and the weights were 0.1559, 0.1560, 0.1557.

Silver.

The silver used was from a quantity prepared many years ago, and whose high degree of purity has been many times proved. In its preparation the chloride was reduced, and the finely divided silver was fused into large masses and electrolyzed in nitric acid solution. The electrolytic silver was fused into buttons on charcoal made from sugar.

Buttons of this silver of suitable sizes were dissolved in nitric acid and the excess of acid was driven off on the water bath. Water and an excess of perchloric acid were added and the water was evaporated. The evaporation was repeated twice. Experiments already described indicate that there remained only a trace of nitric acid, too small to influence the results. The perchlorate was dissolved in 150 cc. of water, and the solution was subjected to electrolysis with a voltage of 3 and current strength 0.2. The revolving electrode was used, but as silver oxide accumulated in considerable amount the rate of the anode was lowered and in some cases stopped for a time to prevent the throwing off of this oxide. In experiment 3 the temperature was kept at 60° during the electrolysis, to hasten the solution of the oxide. In all cases it was completely dissolved from the anode long before the current was stopped. In each case the current was continued till after the acid solution had been siphoned off and replaced by water. The following are the data:

	Silver taken.	Silver found.	Acidity.
1.....	0.1836	0.1836	0.1 N
2.....	0.2112	0.2112	0.06 N
3.....	0.1637	0.1636	0.4 N

Cadmium.

The cadmium used was in the form of oxide, made by Merck. It contained water, but tests failed to disclose any other impurities save a trace of lead. It was heated for an hour in a porcelain boat in a tube through which oxygen was passed. Portions were weighed in the dish to be used in the electrolysis and dissolved in a small excess of perchloric acid. The solution was made up to 150 cc. The current was started at 3.5 volts and 0.3 ampere per square decimeter of cathode surface. Later it was increased to about 0.5 ampere. The time was three hours. The cadmium formed a fairly compact layer save near the center of the dish where the anode was nearer the dish and where the movement of the solution was smaller. Like the silver, it was sufficiently adherent at all points to avoid danger of loss in washing. Three experiments gave the following values:

	Cadmium oxide.	Cadmium calculated.	Cadmium found.	Acidity.
1.....	0.3332	0.2917	0.2896	0.08 N
2.....	0.2131	0.1865	0.1857	0.03 N
3.....	0.2630	0.2302	0.2291	0.033 N

Of course little could be claimed for the purity of the cadmium oxide used, and its cadmium content was, therefore, determined by two of the older methods. In Experiment 4 the oxide was dissolved in a small excess of sulfuric acid and three grams of pure sodium acetate were added. In Experiment 5 the oxide was dissolved in pure perchloric acid and three grams of pure potassium cyanide were added. This gave a better deposit than those obtained in the other experiments with cadmium. In all cases there seems to be a trace of cadmium remaining in solution, as shown by a slight yellow color rather than a distinctly visible precipitate when the solutions after electrolysis are treated with hydrogen sulfide.

	Cadmium oxide.	Cadmium calculated.	Cadmium found.
4.....	0.2937	0.2571	0.2537
5.....	0.2716	0.2378	0.2356

As may be seen, the cadmium found in these two experiments is on the average about 1.5 milligrams smaller than that found in Experiments 1, 2 and 3. The source of this difference is as yet not clear, but it seems very probable that cadmium may be as completely separated electrolytically from dilute perchloric acid as from any other solvent.

Work is in progress on the practicability of using perchloric acid in depositing other metals.

THE STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION BY SODIUM OXALATE.¹

BY R. S. MCBRIDE.

Received February 7, 1912.

I. Introduction: 1. Object of the Research. 2. Considerations Affecting the Choice of a Standard. 3. Reasons for the Choice of Sodium Oxalate. 4. Normal Course of the Reaction. II. Experimental Work: 1. Reagents Employed. 2. Weighing of Oxalate and Permanganate Used. 3. Effect of Conditions upon the Result of a Titration. *a.* End-point Corrections. *b.* Rate of Addition of the Permanganate. *c.* Volume of the Solution. *d.* Acidity and Temperature. *e.* Air Access—Oxidizing Effect. *f.* Presence of Added Manganous Sulfate. III. Discussion and Conclusions: 1. Review of Possible Errors. (*a*) Loss of Oxalic Acid by Volatilization. (*b*) Decomposition of Oxalic Acid by Water. (*c*) Decomposition of Oxalic Acid by Sulfuric Acid. (*d*) Oxidation of Oxalic Acid by the Air. (*e*) Presence of Oxalic Acid Unoxidized at the End-point. (*f*) Liberation of Oxygen. (*g*) Incomplete Reduction of the Permanganate. (*h*) Impurities in the Oxalate. (*i*) Abnormal Oxidation Products. 2. Summary and Conclusions. 3. Method of Procedure Recommended. 4. Accuracy and Precision Attainable.

I. Introduction.

1. *Object of the Research.*—The standardization of potassium permanganate solutions has been the subject of much study and an excessive amount of controversy. There have been far too many standards proposed for this work to permit one not familiar with the subject to select the best; and, in fact, it is doubtful whether or not any one of those standards proposed can in all senses be considered the best. However, the work of the Bureau of Standards has demanded that some substance be selected for this use, which could be employed with a certainty of a reasonably correct result. It was desired, if possible, that the standard selected should serve a threefold purpose, *viz.*, first, as a primary standard of oxidimetry; second, as a working standard for regular use in our own laboratories; and third, as a substance which could be distributed by the Bureau with a guarantee both as to its purity and as to its reducing value when used under specified conditions.

Although the voluminous literature relating to the standardization of potassium permanganate solutions has been examined with considerable care, it is not thought desirable to give a history of the subject, or even a bibliography. None of the theories considered here are new; but it is hoped that the experimental facts presented will be of value as a guide to the proper use of sodium oxalate as a standard.

2. *Considerations Affecting the Choice of a Standard.*—It is seldom that a single measure can be used both as a primary reference standard and as a regular working standard; but for some volumetric work this is possible. To serve any such double function, a substance must meet the following conditions:

¹ Published by permission of the Director of the Bureau of Standards.

(a) There must be reasonable ease of preparation and accurate reproducibility.

(b) The purity must be determinable with sufficient accuracy; and the purified material must be stable under ordinary conditions of the laboratory.

(c) The use of the material in regular work must demand neither complex apparatus nor difficult manipulations.

(d) Such precision must be obtainable when it is used with ordinary care that one, or at the most a very few determinations suffice for the fixing of the value of a standard solution.

(e) The accuracy obtained under ordinary conditions of its use in standardization must be at least as great as that required in the use of the solution to be standardized.

3. *Reasons for the Choice of Sodium Oxalate.*—In the above five respects, it appeared that sodium oxalate was probably best suited to our needs; and a detailed study of this standard was undertaken.

The methods of preparation and testing of sodium oxalate have been carefully studied by Sørensen.¹ In continuation of such study, Mr. J. B. Tuttle and Dr. Wm. Blum, of this laboratory, have carried out several important lines of work; and at the request of the Bureau of Standards, several firms of manufacturing chemists have improved their methods of preparation of sodium oxalate on a large scale. At this point it is sufficient to state that all of this work indicates that it can be prepared in a suitable form at reasonable expense; that it is reproducible; that its purity can be tested readily; and that once purified, it is satisfactorily stable under ordinary conditions.²

The discussion of the other three criteria as to the value of sodium oxalate, *viz.*, convenience, precision and accuracy, forms the subject of the present article.

In advance of the general discussion it is not amiss to state the conclusions drawn as to these three points. It appears that, when the conditions for the use of the sodium oxalate have been defined, they may be conformed to easily and no unusual apparatus or complex procedure is necessary. The accuracy obtainable is, within the limits of our present knowledge, sufficient for even the most refined work (see p. 415); and the precision or agreement of duplicates is satisfactory.

Along with such striking advantages we find certain disadvantages, but none of these appear serious. The more important are as follows:

(a) The largest sample which can be used ordinarily (for 50 cc. of 0.1 *N* KMnO_4) is only 0.3 gram. This necessitates an accurate weighing in order to gain a high degree of accuracy. It is not desirable to use a stand-

¹ *Z. anal. Chem.*, 36, 639; 42, 333 and 512.

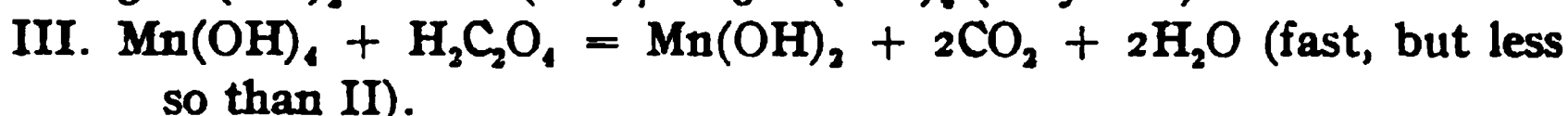
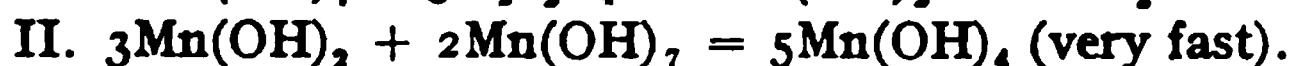
² See Blum, *THIS JOURNAL*, 34, 123 (1912).

ard stock solution, unless freshly prepared. If such solution is kept for any considerable length of time, it acts upon the glass of its container; it is also slowly decomposed by the action of light.

(b) The detection of small amounts of allied organic compounds in the sodium oxalate is rather difficult, except by comparison of the reducing value with that of other samples of known purity.

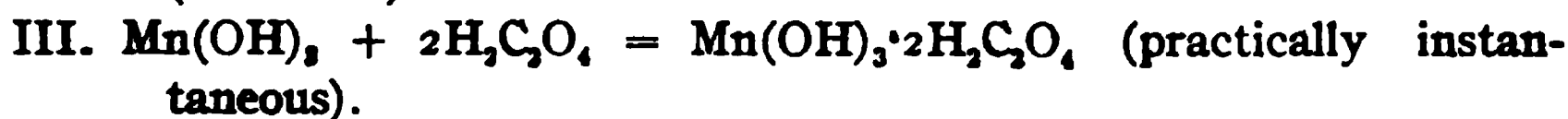
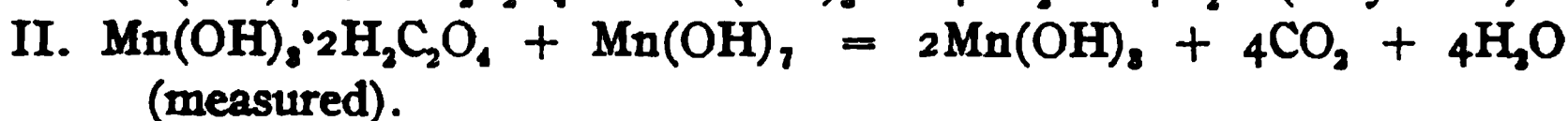
(c) The initial drying of the oxalate is subject to slight uncertainty; but once dried it is practically non-hygroscopic.

4. *Normal Course of the Reaction.*—In 1866 Harcourt and Esson¹ concluded from a study of the speeds of reaction under various conditions, that the steps of the reaction are as follows:

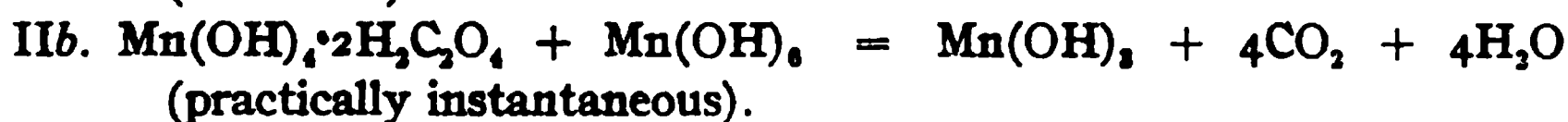
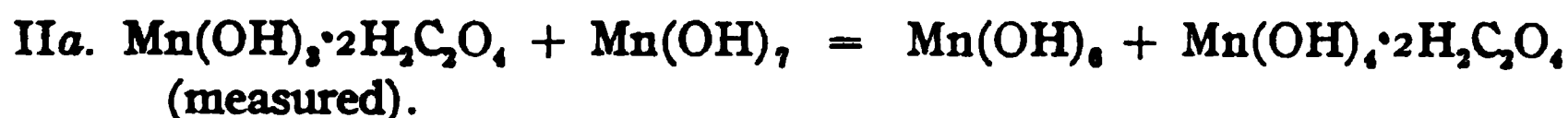


Among the more recent articles presenting either experimental or theoretical evidence on this subject, the more important are those by Schilow² and by Skrabal.³

From measurements of the speeds of reaction, the former presents the following system as representing the steps of the reaction:



The second of these can be divided into two parts:



However, this author qualifies the proposed explanation by the following statements:

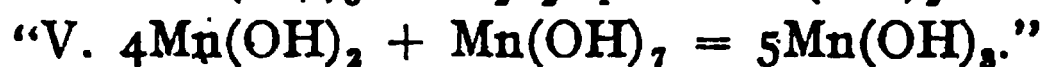
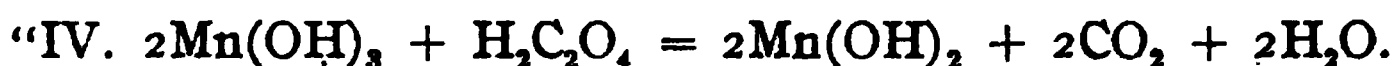
"This scheme is considered only as an approximate picture of the phenomenon and is true particularly for mean concentration of hydrogen ions and low temperatures (0–25°). Under other conditions, side reactions and disturbances enter in, which can be partially observed or foreseen.....

"In addition to the reactions given above, the following two also require consideration:

¹ *Phil. Trans.*, 156, 193.

² *Ber.*, 36, 2735 (1903).

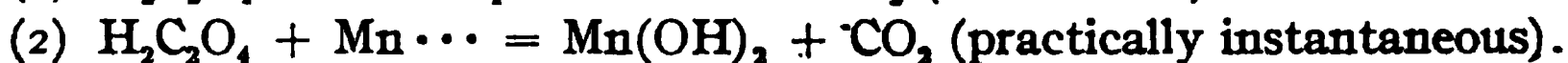
³ *Z. anorg. Chem.*, 42, 1 (1904).



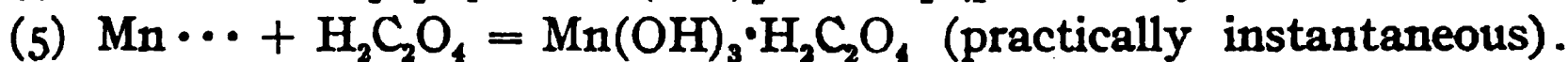
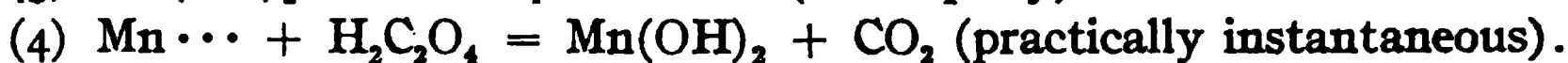
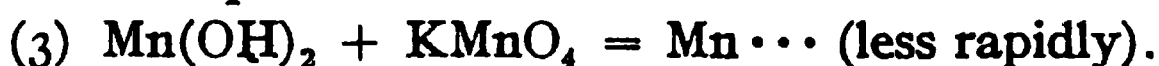
These last reactions, however, are not assigned a definite role in the general scheme.

After an extended series of experiments on the speed of the reaction under various conditions, Skrabal¹ advances the following scheme as representing the course of the reaction:

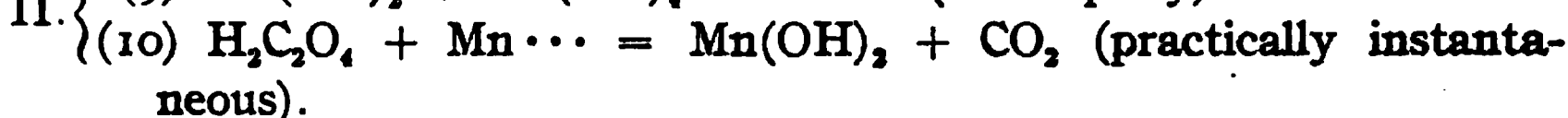
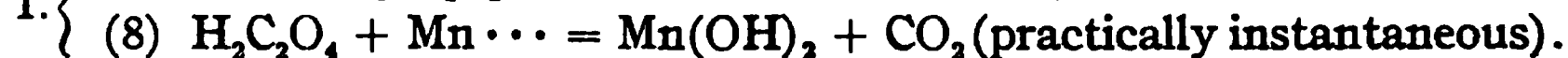
Incubation period:



Induction period:



End period:



Since this last system of reactions is based upon elaborate experimental work it can be accepted as probably best representing the normal course of the reaction. For the present considerations any one of the systems would serve equally well to explain the observed facts.

The variations from a normal course will be considered after the experimental part of the present work has been described.

II. Experimental Work.

1. *Reagents Employed.*—The water and sulfuric acid employed were frequently tested for reducing matter, and in each case were shown to be free from appreciable amounts of such impurities. The manganous sulfate was similarly tested for reducing and oxidizing influence and shown to be satisfactory. To purify the air used for the tests of Tables VI and VII, it was passed through cotton wool to remove dust and grease, bubbled through a solution of potassium hydroxide to take out any acid vapors present and then through solutions of chromic acid and potassium permanganate. The purified air had no detectable reducing effect upon dilute solutions of permanganate under the conditions of titration.

The carbon dioxide used for the tests of Table VI was taken from a cylinder of the commercial liquid and passed through water, chromic acid and permanganate solution before use. An analysis showed the

¹ *Loc. cit.*

presence of about 3% of methane; but this gas seemed to have only a very slight reducing action on the permanganate in dilute solution, so that the results of the series in which it was used can be regarded as but slightly less reliable than the series in Table VII. For this latter group of tests, pure carbon dioxide was made from acid and sodium carbonate. This source gave a gas which had no detectable reducing action under the conditions of its use.

The potassium permanganate used for most of the work was a sample of good quality which had been made up in normal solution for over six months before filtration and dilution to tenth-normal strength for use. The diluted solution was filtered frequently through asbestos to ensure freedom from precipitated manganese dioxide. For the series of tests reported in Table IVb, a second permanganate was used. In this case the strong solution was boiled for a few minutes, cooled, filtered and diluted to tenth-normal strength. For the series of Table VII, still a different permanganate was employed, this stock being prepared in the same manner as the main solution. About 40 grams of solution were used for each titration.

The sodium oxalate used for all of the experiments except those of Table IVb was a sample specially purified in this laboratory by Mr. J. B. Tuttle. It is sufficient to state here that all tests indicated a total impurity of not over 0.05%. For the tests of Table IVb, another sample of sodium oxalate made by the Mallinckrodt Chemical Works, especially for our use, was employed. This material was shown by test to be as pure as that prepared in our own laboratory.

2. *Weighing of Oxalate and Permanganate Used.*—Since in all of the work described in the following part of this article only comparative values were required, the absolute amount of oxalate employed in any one test was not of importance, as long as the relative amounts present in the experiments of a series were accurately known. Therefore it was found desirable to use about a 20-gram portion of a 0.2 *N* stock solution of the oxalate for each test. Each such sample was weighed from a buret to the nearest 5 mg.; the relative weight of each sample was thus determined to better than one part in 3000, in less time and with greater certainty than would have been possible by weighing out the dried powder.

In order to prevent any change in the strength of the stock solution from affecting the conclusions drawn from the results of any series of titrations, only those values obtained during a period of a few days are compared with each other. This plan avoided any uncertainty due either to slow decomposition of the oxalate in solution, occurring through action on the glass of the container or oxidation by the air through the aid of light, or to change in oxidizing value of the permanganate solution employed.

The measurement of the permanganate solution was accomplished by the use of a weight buret. For this work, this form of instrument possesses the following advantages: (a) Correction for the temperature changes which affect the volume of the solution, is not necessary; (b) completeness or uniformity of running down of the solution from the buret walls, is unessential; and (c) the solution can be weighed readily to 0.01 g. (1 part in 5000 on a 50 g. sample), whereas measurement to 0.01 cc. is exceedingly uncertain. The freedom from errors due to temperature changes is of great importance in this work, as the buret is often very appreciably warmed by the steam rising from the hot liquid undergoing titration.

The buret used was made from a 50 cc. cylindrical separatory funnel by drawing down the stem to the form of an ordinary buret tip. For exact work it has been found desirable to have this tip so drawn down that it will deliver about 10 cc. per minute or 0.03 cc. per drop.

3. *Effect of Conditions upon the Result of a Titration.*—The ordinary procedure for the use of sodium oxalate in the standardization of potassium permanganate is as follows: Dissolve about a quarter of a gram of the oxalate in 250 cc. of water, acidify with sulfuric acid, warm to 70° and titrate to the first permanent pink.

It was desirable to determine the effect of the variation of the following conditions upon the result obtained, *viz.*, temperature, acidity, volume of solution, rate of addition of the permanganate, access of air, presence of added manganous sulfate and, in connection with these, the corrections necessary upon the apparent end points. In order to accomplish such determinations, the factors were varied one at a time, noting the difference, if any, produced upon the apparent value of the permanganate. The results of the titrations are reported as the ratios of the oxalate used to the permanganate used multiplied by 10^{-2} . These values are proportional to, and, indeed, numerically almost equal to, the iron value of the permanganate. Therefore, for purposes of discussion the values are treated as if they were the iron value of the permanganate, expressed in grams of iron per gram of solution. It should be noted that an increase in the iron value represents a decrease in the permanganate consumed, and *vice versa*. A variation of 0.01 cc. in the amount of permanganate used in a titration is approximately equivalent to a change of one unit in the last expressed figure of the iron value.

a. *End-point Corrections.*—In a recent article Dr. W. C. Bray¹ has suggested the necessity for the correction of the apparent end-point obtained in the reaction of oxalic acid and permanganate, and has recommended that the correction be determined as follows: After reaching the end-point, the solution is cooled to room temperature, potassium iodide

¹ THIS JOURNAL, 32, 1204 (1910).

solution is added, and the iodine liberated is at once titrated with dilute (0.02 *N*) sodium thiosulfate.

In order to test the necessity and the accuracy of this method under the various conditions of titration, we examined experimentally the following points:

(a) Does the equivalent in oxidizing power of the permanganate excess remain in the solution long enough to allow the necessary cooling before the titration with thiosulfate?

(b) Does the thiosulfate titration give the total permanganate excess used to produce the end point, or does it indicate only the permanganate which remains in the solution as such?

(c) Does the depth of the pink color at the end of the titration show how great an excess of permanganate has been added in order to produce that end-point?

Before applying the method of correction proposed by Bray, it is necessary to cool the solution to room temperature. Therefore, if, as is desirable, the permanganate end-point is obtained while the solution is hot, some time must elapse during cooling and it is possible that a loss of oxidizing (or iodine liberating) power would occur, which loss would render the correction as subsequently determined valueless. This point was tested by determining the residual oxidizing power of solutions to which had been added known amounts of permanganate at various temperatures (30–90°), with varying acidities (2–10% by volume H_2SO_4) and with the addition of various amounts of manganous sulfate (up to 1 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$). These experiments showed that no appreciable loss occurred within a period of one-half hour, if only a small amount of permanganate (0.02–0.20 cc. of 0.1 *N* soln.) is added to any such solution. Moreover, this condition was found to exist even when the permanganate was wholly decolorized by reaction with the manganous salt. The full oxidizing power was then retained in the solution, probably in the tri- or tetravalent manganese salts (Mn^{+++} or Mn^{++++}). The lapse of 5–10 minutes necessary for cooling the solution to room temperature is thus shown to be without influence; and it is evident that the procedure described determines not only the permanganate remaining in the solution as such, but also that which was not completely reduced to the manganous condition.

The procedure described by Bray has been accepted on the above basis as giving a determination of the real excess of permanganate which was added to produce the end point. However, the question as to the difference between this end point correction and that determined by the depth of the pink color at the end point must be considered on a different basis.

For each of the titrations made in this investigation, two values were

obtained, the one using the color method, the other the iodine method for correction of the total permanganate added. In several of the tables below both of these values are reported. By inspection of these data (Tables II, III and V) it will be apparent that, in general, the color correction and the iodine correction differ by no more than 0.02 cc., except when the end-point was reached with the solution at temperatures below 35°, or when the permanganate solution was added rapidly just at the end-point. This was true in all but six of over two hundred tests; and even in these, the difference between the two corrections was not more than 0.04 cc. It is, therefore, certain that if the end-point is approached slowly in a solution above 60° the depth of color will be proportional to the total excess of permanganate added, *i. e.*, no permanganate will be decolorized without at the same time being completely reduced to the manganous condition. However, at lower temperatures, in the presence of much sulfuric acid (more than 5% by volume), and particularly with rapid addition of permanganate or with insufficient stirring just preceding the end-point, the amount of permanganate decolorized but not wholly reduced to the manganous condition may easily be as much as 0.1 cc.

b. Rate of Addition of the Permanganate.—The rate of addition of the permanganate solution in the titration of iron in solutions containing chlorides has been shown to have considerable effect upon the result obtained.¹ The influence of this factor upon the oxalate-permanganate reaction was, therefore, studied.

The influence of varying the amount of permanganate added before the quick color changes of rapid reduction began was first tested. This factor has an influence only at low temperatures (below 40–50°) as at any higher temperature the reduction proceeds rapidly from the very start. Tests made at 30° in 5% sulfuric acid solution gave results as follows:

Amount of KMnO_4 added before rapid decolorization was evident.....	3.0 cc.	10.0 cc.	25.0 cc.	40.0 cc.
Results obtained (strength of KMnO_4).....	0.005936	0.005936	0.005932	0.005929
	37	35	33	
	34	37		

These results show that the addition of a large amount of permanganate before rapid oxidation of the oxalate begins tends to give lower values for the permanganate solution, *i. e.*, to cause a larger consumption of permanganate. The influence of this factor is small, but it is of some significance, as will be apparent from the later discussion.

¹ Skabarl, A., *Z. anal. Chem.*, 42, 359 (1903). Friend, A. N., *J. Chem. Soc.*, 95, 1228 (1909). Jones and Jeffrey, *Analyst*, 34, 306 (1909).

After the initial reduction of 3–10 cc. of permanganate the rate of addition of the main portion of the permanganate was varied, giving the results listed in Table I. These experiments indicate that except on long standing at a high temperature (after starting the reaction), or with a very rapid addition of permanganate to a weakly acid solution at a high temperature, the rate of the addition of the permanganate during the main part of the titration has no influence. The high values obtained in experiments marked * are probably due to oxidation of the oxalic acid by the air; and the low values of experiments marked † show a loss of oxygen, because of the excessive rate of the permanganate addition.

TABLE I.—EFFECT OF RATE OF ADDITION OF PERMANGANATE DURING MAIN PART OF TITRATION.

Acidity, vol. % H ₂ SO ₄ .	Temp.	Time for titration. min.	Result, corrected iron value.	Acidity, vol. % H ₂ SO ₄ .	Temp.	Time for titration. min.	Result, corrected iron value.
5	80°	5	0.005945	2	30°	0.5	0.005592
		5	45			0.5	92
		27 ¹	46			5.0	92
		120 ²	56*			4.0	93
		120 ²	56*			5.0	91
						60 ¹	94
						60 ¹	95
5	30°	7	0.005942	2	90°	0.5	0.005589†
		6	42			0.5	88†
		37 ¹	44			5	98
		120 ²	44			5	5600
						30 ¹	00
						30 ¹	5598

The effect of the rate of the addition of the permanganate just at the end-point has already been suggested (p. 400); but the following data will make this point clearer. In each pair of tests the only variable was the rate of the addition of the permanganate solution just before the end-point. Only the two experiments in each group may be compared (see Table II).

In the first part of Table II some rather extreme cases (experiments done at 30°) have been chosen to show how large the error of the apparent end-point may be, without any influence upon the corrected value. In cases where much smaller corrections were necessary (temperature 60° and above), the agreement of uncorrected values was better, regardless of the speed at which the end point was approached. The latter part of Table II shows this agreement of the uncorrected values at the higher temperature. Nevertheless, it is not desirable to approach the end-point so rapidly as to make a correction larger than 0.1 cc. necessary.

¹ Dropwise, with stirring.

² Intermittent, without continuous stirring.

TABLE II.—EFFECT OF RATE OF ADDITION OF PERMANGANATE AT THE END-POINT.
In the first of each pair of experiments, the end-point was approached slowly, in the second rapidly.

Temp.	Acidity, vol. % H ₂ SO ₄ .	Color blank.	Iodine blank.	Value of permanganate.		
				Uncorr.	Color corr.	Iodine corr.
30°	2	0.01	0.03	0.005584	0.005586	0.005589
		0.25	0.34	37	71	87
30	5	0.03	0.09	0.005929	0.005933	0.005942
		0.15	0.39	5894	12	42
30	5	0.05	0.085	0.005030	0.005034	0.005037
		0.08	0.19	17	26	38
30	5	0.04	0.08	0.005923	0.005929	0.005935
		0.51	5871	..	37.
30	10	0.06	0.11	0.005636	0.005642	0.005648
		0.08	0.14	33	43	50
60	2	0.05	0.05	0.005642	0.005649	0.005649
		0.03	0.05	45	49	51
60	5	0.05	0.07	0.005638	0.005646	0.005649
		0.05	0.06	40	44	46
83	2	0.06	0.07	0.005642	0.005650	0.005651
		0.06	0.06	45	52	52
96	2	0.05	0.04	0.005647	0.005652	0.005651
		0.2	0.15	33	61	54

c. *Volume of the Solution.*—The volume of the solution in which the titration is made might affect the rate of the reaction and, therefore, possibly the result of the titration. Tests were made of this point by varying the initial volume in a series of titrations made at 90° in solutions containing 5% by volume of sulfuric acid. The results were as follows:

Initial volume..	50 cc.	250 cc.	500 cc.	700 cc.	1000 cc.
Values obtained	0.005139	0.005139	0.005136	0.005133	0.005127
	36	39	34	32	29
		37			

By increasing the initial volume beyond 250 cc., the resulting value for the permanganate solution is markedly decreased. That this is due to the change in the initial concentration of the oxalate is indicated by the results obtained in two titrations in which the initial volume was 1000 cc. but the amount of oxalate used was increased threefold, thus making its initial concentration about that ordinarily resulting in an initial volume of 350 cc. The results thus obtained were 0.005136 and 0.005136.

At 30° the initial rate of the permanganate reduction is so much less than at 90°, that it is not possible to note the effect of initial volume free from this influence. A few results were obtained as follows:

Initial volume.....	50 cc.	250 cc.	1000 cc.
Values obtained.....	0.005943	0.005942	0.005945
	45	42	

In these experiments no decided effect of volume is to be found.

It should be noted that in each of these cases the change in volume had no effect upon the concentration of the sulfuric acid present.

d. Acidity and Temperature.—The effects of acidity and of temperature were investigated by two series of experiments, the results of which are given in Tables III and IV. These data show that either higher temperature or less concentration of sulfuric acid tends to give higher values for the permanganate, *i. e.*, to reduce the amount of permanganate required. These effects are not large and, indeed, the results obtained in some cases show duplicates as discordant as experiments carried out under somewhat different conditions; nevertheless, the tendency in the two directions is rather convincing that these factors have a real influence upon the results obtained. The importance of even such slight variations is considerable, as will be apparent from the discussion later.

It will be seen from the data of Table IV that the first series exhibits a larger apparent influence of temperature than the second series reported. This is due to the greater care exercised in the latter series to stir the solution very vigorously and to add the permanganate more slowly, particularly at the beginning and end of each titration. However, the first series shows better the variation which may be expected if only ordinary titration precautions are observed.

TABLE III.—EFFECT OF ACIDITY AND TEMPERATURE.

Temp.	Acidity, vol. % H ₂ SO ₄ .	Color blank.	Iodine blank.	Value of permanganate.		
				Uncorr.	Color corr.	Iodine corr.
30°	2	0.04	0.06	0.005129	0.005135	0.005137
	2	0.04	0.05	33	38	39
	5	0.04	0.05	27	32	34
	5	0.03	0.035	27	31	31
	10	0.05	0.10	18	25	32
	10	0.02	0.09	21	24	33
	10	0.02	0.09	21	24	33
45	2	0.02	0.03	0.005134	0.005136	0.005138
	2	0.03	0.04	34	38	40
	5	0.03	0.04	30	34	35
	5	0.03	0.025	30	37	36
	10	0.01	0.03	35	36	39
	10	0.03	0.03	31	35	35
	10	0.02	0.035	37	40	42
60	2	0.02	0.02	0.005129	0.005132	0.005132
	2	0.03	0.03	36	40	40
	2	0.035	0.035	33	37	37
	2	0.04	0.05	35	41	42
	5	0.04	0.06	26	32	46
	5	0.05	0.05	32	39	39
	10	0.05	0.05	33	40	40
	10	0.03	0.05	33	37	40
	10	0.02	0.04	34	38	40
	10	0.02	0.04	34	38	40

TABLE III (continued).

Temp.	Acidity, vol. % H ₂ SO ₄ .	Color blank.	Iodine blank.	Value of permanganate.		
				Uncorr.	Color corr.	Iodine corr.
75°	2	0.03	0.02	0.005141	0.005144	0.005143
	2	0.03	0.03	37	41	41
	5	0.04	0.025	37	42	40
	5	0.03	0.03	39	43	43
	10	0.05	0.06	29	36	37
	10	0.06	0.04	34	43	40
80	2	0.05	0.045	0.005138	0.005145	0.005144
	2	0.02	0.03	36	39	40
	2	0.04	0.05	36	42	43
	5	0.03	0.05	38	42	44
	5	0.04	0.04	39	44	44
	10	0.03	0.03	34	38	38
	10	0.03	0.03	36	40	40
86	2	0.04	0.03	0.005142	0.005146	0.005144
	2	0.02	0.03	40	43	43
	5	0.03	0.035	38	42	43
	5	0.02	0.02	37	40	40
	10	0.02	0.02	38	41	41
	10	0.03	0.045	35	39	41
92	2	0.02	0.03	0.005143	0.005146	0.005148
	2	0.02	0.03	46	48	49
	5	0.035	0.04	39	43	44
	5	0.05	0.05	32	39	39
	5	0.05	0.06	30	37	39
	5	0.06	0.06	31	39	39
	10	0.05	0.05	32	38	38
	10	0.06	0.06	30	38	38

TABLE IV.—EFFECT OF ACIDITY AND TEMPERATURE.

(a) Series 1, rearrangement of data of Table III.

Temperature.	Acidity, vol. % H ₂ SO ₄ .		
	2%.	5%.	10%.
30°	0.005138	0.005133	0.005132
45	39	35	38
60	38	42	40
75	42	42	38
80	42	44	39
86	44	42	41
92	48	40	38

(b) Series 2.

30	0.005646	0.005646	0.005649
60	50	48	48
80	..	50	..
85	51	50	44
92	..	50	..
95	53	52	46

Each value reported is the average of at least two determinations.

In addition to the data of Tables III and IV, those in other tables will show the same influence of temperature and acidity as are here indicated. Taking these data all together, it is certain that, though small, these influences are appreciable.

The time in the titration at which the temperature has an influence upon the result is evident from the tests of Table V. These data show that, except in its influence upon the size of the end-point correction, the temperature of the solution after the first few cc. of the permanganate have been decolorized is without appreciable effect. The significance will be apparent when considered in connection with the results of the tests given in Table VIII.

TABLE V.—TIME AT WHICH TEMPERATURE HAS EFFECT.

All titrations started in 250 cc. of 5% by volume sulfuric acid.

Temperature: a, initial; b, during main part of titration; c, at end-point.			Value of permanganate.				
a.	b.	c.	Color blank.	Iodine blank.	Uncorr.	Color corr.	Iodine corr.
90°	90°	90°	0.05	0.06	0.005130	0.005137	0.005139
			0.06	0.06	31	39	39
90	90	30	0.03	0.07	29	33	38
			0.03	0.065	30	34	39
90	30	30	0.03	0.09	25	29	37
			0.04	0.12	19	24	35
30	30	30	0.03	0.05	0.005126	0.005130	0.005133
			0.05	0.08	24	32	36
			0.04	0.085	22	27	32
30	30	90	0.05	0.06	25	31	33
			0.07	0.09	25	34	36
			0.05	0.05	25	30	30
			0.04	0.05	29	34	34
30	90	90	0.03	0.03	29	34	34
			0.03	0.03	31	35	35

e. Air Access—Oxidizing Effect.—It has been suggested¹ that during the course of the reaction atmospheric oxygen, through the carrying action of the manganous salt, might cause the oxidation of appreciable amounts of oxalic acid. To test this point, a preliminary series of experiments was made as to the results obtained on the removal of the larger part of the air from the titration vessel. To accomplish this, the solution to be titrated was made up in a flask with recently boiled water and a small amount of sodium carbonate added just before starting the titration. The carbon dioxide evolved carried out the bulk of the air, and the flask was kept stoppered and the permanganate run in through a small funnel, which passed through the stopper. From the results it

¹ Who first suggested this is not known; Schröder has tested this point recently (*Z. öffent. Chem.*, 16, 270 (1910)). See p. 409 for discussion of his data.

appeared that no oxidizing action of the air was to be feared; but to further test this point the following method was employed.

The solution to be titrated was placed in a glass-stoppered flask of special form (see Fig. 1) and a strong current of air or carbon dioxide, as desired, was bubbled through the liquid before commencing the titration and during its progress. When carbon dioxide was used, the solution was heated to boiling and then cooled to the desired temperature in a stream of the gas, thus ensuring the absence of all but the last traces of air.

The two series of tests made in this manner are summarized in Tables VI and VII:

TABLE VI.—EFFECT OF ACCESS OF AIR ON TITRATION.

All titrations started in 250 cc. of 5% by volume H_2SO_4 .

Temp.	Titration in flask with air bubbled through solution.	Titration in flask with carbon dioxide ¹ bubbled through solution.	Titration in beaker open to air, as in ordinary procedure.
30°	0.005041	0.005037	0.005040
	40	38	39
60	42	40	41
	42	43	40
90	42	47	41
	41	51	44

TABLE VII.—EFFECT OF ACCESS OF AIR ON TITRATION.

All titrations started in 250 cc. of 2% by volume H_2SO_4 .

Temp.	Titration in flask with air bubbled through solution.	Titration in flask with carbon dioxide bubbled through solution.	Titration in beaker open to air, as in ordinary procedure.
30°	0.005591	0.005592	0.005591
	91	93	92
60	94	99	97
	94	99	97
90	94	5600	98
	95	01	5602

The data of Tables VI and VII show that no large error comes from atmospheric oxidation of the oxalate during titration. The largest difference between results obtained using air and using carbon dioxide are only one part in 500 (0.2%) and the differences were usually less than one-half this amount. Moreover, if carried out in a beaker as ordinarily done, the values obtained are not appreciably different from those where air is wholly excluded (cf. last two columns of Table VII); and even when air is bubbled through the solution during a titration at 90°, the oxidation is scarcely appreciable. No such chance for atmospheric action is

¹ The carbon dioxide used in the experiments of Table VI was found to contain 3% of methane, so the results of the tests reported in this table are only approximate. See p. 396.

met with under the ordinary conditions of titration, since when following the usual procedure the carbon dioxide formed during the reaction prevents much oxygen from the air remaining in the solution during the reaction.

One other point tested was the effect of time elapsing before the beginning of the titration. Four samples were made up to 250 cc. with 5% by volume sulfuric acid and heated to 90°. Two were titrated at once, the other two after standing an hour at 90°. The four results agreed within 1 in 5500, showing that even under these rather severe conditions oxalic acid is sufficiently stable and non-volatile to prevent loss during a titration from oxidation (in the absence of manganous salts, at least), from decomposition by the sulfuric acid, or from volatilization with the steam.

As a further proof that atmospheric oxidation is not an important factor in the oxalate titration, the effect of the rate of titration may be cited. In the data of Table I, the titrations covering a period up to one hour show almost no tendency to give higher values.

This is contrary to what might be expected if oxidation were taking place, as the oxidation occurring would naturally be, at least roughly, proportional to the time elapsed; and such is not the case. Experiments marked * are the only exceptions met with (see Table I).

f. Presence of Added Manganous Sulfate.—Since the presence of added manganous sulfate would probably influence the initial rate of the reaction, its effect upon the result of the titration was tested. A series of tests (all but the last two at 30°) was carried out with the addition of manganous sulfate at different points in the course of the reaction. One cc. of the solution of manganous sulfate added was equivalent to the manganous salt formed by the reduction of 10 cc. of the permanganate solution. The results of these experiments are given in Table VIII.

Figure 1



Titration Flask, capacity 500 cc.

It appears from these data that unless the MnSO_4 be added before the beginning of the titration it has little effect upon the result obtained. However, if even a small amount is added before starting the reaction at 30° , the value obtained is the same as is ordinarily obtained at 90° without the addition of manganous salt. Addition before titration at 90° has no influence.

TABLE VIII.—EFFECT OF ADDED MANGANOUS SULFATE.

All but last two tests at 30° , last two at 90° ; all started in 250 cc. of 5% by volume H_2SO_4 .

Amt. MnSO_4 solution added.	Time of addition.	Value of KMnO_4 found.
None	0.0 5576 77 77 79
1 cc.	Before start of titration	0.005582 81
20 cc.	Before start of titration	0.005583 83
1 cc.	After decolorization of 10 cc. of KMnO_4	0.005578 77
20 cc.	After decolorization of 10 cc. of KMnO_4	0.005578 80
1 cc.	Just before end-point	0.005579 81
20 cc.	Just before end-point	0.005578 78
None (titrn. at 90°)	0.005582 83

III. Discussion and Conclusions.

1. *Review of Possible Errors.*—As the standardization procedure consists in solution of a weighed sample in dilute sulfuric acid and direct titration with permanganate, any error occurring must be due either to error in weighing of oxalate or measuring of the permanganate or to a variation of the reaction itself from the form usually given, viz.:



Since as already indicated (p. 397) there is no necessity for an error in either the weighing of the oxalate or the measuring of the permanganate greater than one part in 2000, only the irregularities of the reaction need be considered at length.

The variations of the reaction from its normal course may tend to cause the use of an excess of either permanganate or oxalate; or both sorts of influences may operate at the same time, in equal or unequal degree. There are nine possibilities of such irregularity; the first five of these would cause too small a consumption of permanganate, the next two

an excessive use of it, and the last two might cause either of these effects.

These possible sources of error are:

- (a) Loss of oxalic acid by volatilization from the solution.
- (b) Decomposition of oxalic acid by water.
- (c) Decomposition of oxalic acid by sulfuric acid.
- (d) Oxidation of oxalic acid by contact of the solution with the air.
- (e) Presence of oxalic acid unoxidized at the end-point.
- (f) Liberation of oxygen during the reaction.
- (g) Presence at the end-point of unreduced permanganate or other compounds of manganese higher than manganous.
- (h) Presence of impurities in the oxalate, either of greater or less reducing power than the oxalate.
- (i) Formation of other products of oxidation than carbon dioxide and water.

(a) *Loss of Oxalic Acid by Volatilization.*—The fact that oxalic acid is readily volatile alone suggests the danger of loss from its solution by vaporization with steam. However, from the dilute solutions employed for titration purposes, no such losses occur, as has already been shown. The results obtained after an hour's standing at 90° in 5% sulfuric acid solution showed (p. 407) that no loss of oxalic acid had occurred. Similarly, when the titration extended over a period of one hour (Table I, p. 401) or when carbon dioxide or air was bubbled through the solution (Tables VI and VII, p. 406) no such higher values of the permanganate were obtained, as would have resulted had volatilization of the oxalic acid occurred. From these results it is apparent that no appreciable vaporization of oxalic acid will take place during the course of an ordinary titration, which lasts, at the most, only 5–10 minutes.

(b), (c). *Decomposition of Oxalic Acid by Water or by Sulfuric Acid.*—The same data which have shown that no volatilization occurs also prove that the water and sulfuric acid had not caused a decomposition of the oxalic acid. These possible errors can, therefore, be considered improbable under any ordinary conditions of titration.

The experiments reported by Carles,¹ from which he was led to state that at 100° oxalic acid in solution is slowly decomposed with the formation of carbon dioxide and formic acid, are not confirmed by our experiments. If such decomposition does take place, it is so slow as to have no appreciable influence upon the results of a titration made at 90° or below.

(d) *Oxidation of Oxalic Acid by the Air.*—Schroeder² has shown that in the presence of manganous sulfate, oxalic acid solutions are oxidized by the air at an appreciable speed. This author presents a large amount

¹ Bull. soc. chim., 14, 142–4 (1870).

² Z. öffent. Chem., 16, 270 (1910).

of experimental data, from which he draws very decided conclusions. Those which are of importance in the present discussion are as follows (numbered as in original):

(3) "In the oxidation of oxalic acid by potassium permanganate, an error (too little KMnO_4 used) enters through the presence of atmospheric oxygen, which error is greater in the presence of manganous sulfate or more especially titanium dioxide.

(5) "By rapid titration in a stream of oxygen this error of No. 3 disappears, the oxygen acting on the oxalic acid to give hydrogen peroxide, which requires a corresponding amount of permanganate.

(6) "In the presence of much manganous sulfate, with oxalic acid of high concentration, especially in the presence of titanium dioxide, this hydrogen peroxide of No. 5 disappears, very rapidly if hot, and the error of No. 3 is then evident, as the compensating action of the hydrogen peroxide is not possible.

(7) "Rapid titration at 50° with 30 cc. of 1 : 1 sulfuric acid in 200 cc. of water gives results which agree with the iodine method of standardization."

Schroeder therefore recommends that the greater part of the permanganate be rapidly run into a strongly acidified solution of the oxalate and then the titration finished more slowly. Addition of manganous sulfate is not recommended.

The experimental data presented by Schroeder, which are of importance to this discussion, are those in his tables numbered 3, 4, 5, 6, 10 and 11. These data, with very few exceptions, seem to warrant the following conclusions (not expressed by Schroeder but drawn from his data):

(a) High temperature tends to cause a smaller permanganate consumption (Tables 3, 4, 5 and 6).

(b) High acidity tends to cause a high permanganate consumption (Tables 3, 4, 5, 10 and 11).

(c) Slow titration (10 min.) requires less permanganate than fast ($1-1\frac{1}{2}$ min.) titration.

(d) Presence of added manganous sulfate (1-5 g.) tends to cause less permanganate to be used, even with rapid titration (Tables 5 and 6).

(e) Titration in an air current required slightly more permanganate than in a current of carbon dioxide, when made either rapidly or slowly or in the presence of large or small amounts of acid.

It must be noted that in his experiments the stirring was very inefficient, since Schroeder often refers to his titration as "frequently whirled" (*umgeschwenkt*) and "whirled from time to time;" and no end-point corrections were made even when the titrations were conducted rapidly, at low temperature, or in the presence of large amounts of acid and manganous salt.

These conclusions as to the influence of conditions are confirmed, in general, by the data obtained in our own work; but it does not seem that the conclusions expressed by Schroeder (quoted p. 410) necessarily follow from the data which he presents. In fact, from his own experimental results, we would infer, as stated by us in our conclusion (e) (2nd preceding paragraph), that the error due to atmospheric oxidation claimed by him (see (3) p. 410) does not exist. Although it is admitted that on long standing at high temperature oxalic acid in solution in the presence of much manganous sulfate is oxidized by the air, such a combination of conditions is not met in the standardization of permanganate; and such oxidation does not take place to any such extent as claimed by Schroeder under the conditions which are properly employed. On the above basis we believe that Schroeder's conclusion (3) is not warranted, even by his own data.

If, as seems necessary, the explanation that loss of oxygen and not atmospheric oxidation is responsible for the variation of the permanganate values obtained under different conditions of titration, then the conclusions (5) and (6) expressed by Schroeder are not necessary for the explanation of the experimental data.

The fact that the use of the conditions chosen by Schroeder gave values which agreed well with those obtained by the iodine method of permanganate standardization (see (7) p. 410) would not prove that these conditions are correct, since no evidence is presented to show that the iodine standardization was carried out under conditions giving correct values. As a matter of fact, the iodine standardization is even more largely affected by conditions than is the oxalate method and none of these influences has been systematically studied.

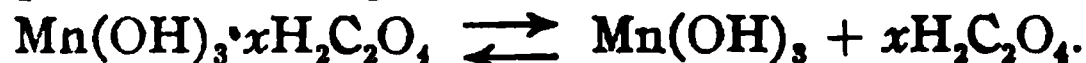
As has already been stated (p. 406) the experimental data obtained by the author do not indicate that any appreciable atmospheric oxidation of oxalic acid occurs during the course of a standardization. Moreover, Schroeder's data warrant the conclusion that when titrations are made in a stream of air, no less (and perhaps even more) permanganate is required than if made in a stream of carbon dioxide.

Therefore, it appears certain that the oxidizing effect of the air during the permanganate-oxalate reaction will not have an appreciable influence upon the result obtained from such standardization.

(e) *Presence of Oxalic Acid Unoxidized at the End-point.*—In so far as our present knowledge goes, there is no evidence to indicate any incompleteness in the oxidation of the oxalic acid. Since one of the products of the reaction, the carbon dioxide, is almost wholly removed from the sphere of action, there is little if any tendency to come to an equilibrium before the whole of the oxalate is oxidized. The reaction

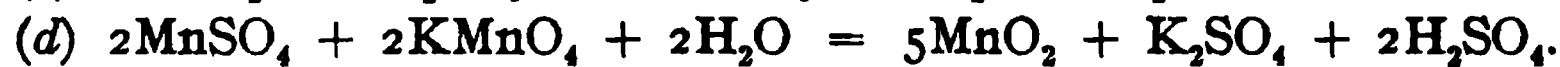
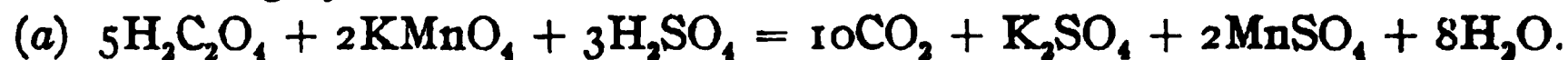


cannot be reversible under the conditions of titration; and unless it be reversible, unoxidized oxalic acid would hardly remain in the presence of an excess of permanganate. Moreover, if no free oxalic acid remains, the complex $\text{Mn}(\text{OH})_3 \cdot x\text{H}_2\text{C}_2\text{O}_4$ could not be stable since it would be completely decomposed according to the reaction



Since the $\text{H}_2\text{C}_2\text{O}_4$ formed by this last reaction is destroyed by the KMnO_4 excess as fast as formed, the reaction would continue to the complete decomposition of the complex. The fact that the solution at the end of a titration contains an excess of permanganate and does not lose its oxidizing power, even after standing for half an hour or more at 90° , indicates that the oxidation of the oxalate must have been complete during the titration.

(f) *Liberation of Oxygen*.—In a recent article Sarkar and Dutta¹ claim that unlimited amounts of permanganate can be reduced by small amounts of organic material at high temperatures ($85\text{--}90^\circ$) and high acidity by the following cycle of reactions:



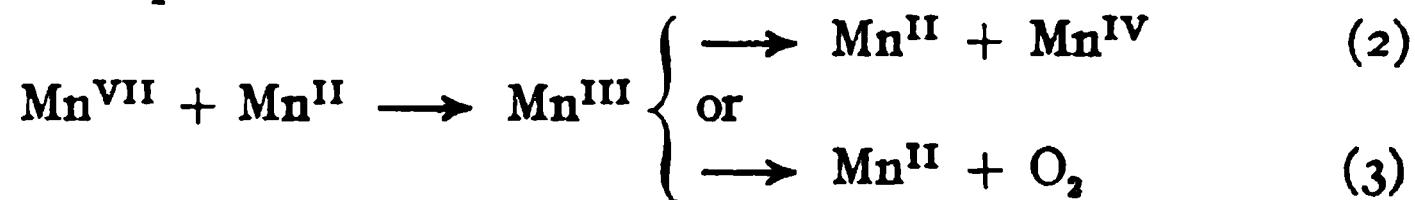
Similarly other authors have claimed that oxygen is evolved from the interaction of sulfuric and permanganic acids.²

In reply to Sarkar's and Dutta's claim, Skrabal³ has proposed the following scheme as explaining the evolution of oxygen when permanganate and oxalic acid react. (Compare with this author's scheme for the normal reaction, given on p. 396.)

I. Incubation period:



II. Induction period:



III. End period:



Whether one wished to accept this last scheme, or that of Sarkar and Dutta, or even some entirely different explanation, the fact remains that oxygen may be evolved during the course of these reactions when they take place under certain conditions. Such oxygen loss would be ex-

¹ *Z. anorg. Chem.*, **67**, 225–33 (1910).

² Hirtz and Meyer, *Ber.*, **29**, 2828–30 (1896). Gooch and Danner, *Am. J. Sci.*, [3] **44**, 301–10 (1892). Jones, *J. Chem. Soc.*, **33**, 95 (1878).

³ *Z. anorg. Chem.*, **68**, 48–51 (1910).

pected under either of the following conditions, *viz.*, an increased concentration of acid or an increased concentration of HMnO_4 or MnO_2 (and possibly also of Mn_2O_3) in the solution. The first of these conditions is produced by direct increase in amount of acid added and the result has been shown to be an increased permanganate consumption (see Tables III and IV). The presence of HMnO_4 , MnO_2 and perhaps Mn_2O_3 , one or all, is caused by any one of the following influences:

Low temperature, which decreases the rate of their reduction to the manganous condition.

Large bulk of solution, which reduces the oxalate concentration and therefore the rate of their reduction to manganous condition; and

Rapid addition of permanganate (especially at the start or just before the end-point) or insufficient stirring, both of which allow the unreduced or partially reduced manganese to accumulate throughout or in parts of the solution.

Each of these conditions has been shown to cause an increase in the permanganate used for the titration. On the other hand, addition of manganous sulfate, which increases the rapidity of the reduction of the manganese, causes a decreased consumption of permanganate (see Table VIII).

To briefly summarize these points: the loss of small amounts of oxygen, which certainly does occur under some conditions, would account for the effect noted in all of the experiments described where change of temperature, of acidity, of volume, of rate of addition of the permanganate, of rate of stirring or the addition of manganous sulfate has an appreciable influence upon the result of the standardization. Since with proper precautions these variations can be reduced, indeed almost eliminated, over considerable range of temperature, acidity and volume of solution, there is good reason to believe that the loss of oxygen is almost, if not wholly, prevented. In this connection, it must again be emphasized that vigorous stirring throughout the titration, and slow addition of the permanganate at the beginning and at the end, are essential if correct results are to be had.

(g) *Incomplete Reduction of the Permanganate.*—It has been shown in the discussion of the end-point corrections (p. 399) that in addition to permanganate there is often manganic (Mn^{+++}) or tetravalent manganese (Mn^{++++}) salt present at the end-point. However, the error caused by their presence is corrected by the end-point "blank" described above and, therefore, need not be considered as influencing the results already given. In the ordinary titration, such error would be serious only if improper conditions of titration were chosen. The conditions recommended below entirely eliminate this source of error.

(h) *Impurities in the Oxalate.*—The question of purity of the sodium

oxalate, water and acid used in the titration, must, of course, be considered; but there is no need for appreciable error to arise due to this source if the simple tests referred to above under "reagents used" are applied. As especially affecting the present discussion, this source of error has been eliminated even beyond the accuracy of the tests for purity of the oxalate, since only comparative values were employed.

(i) *Abnormal Oxidation Products*.—Several abnormal products of the oxidation can be imagined, for example, carbon monoxide, hydrogen, hydrogen peroxide and oxides of carbon higher than carbon dioxide. It is not at all probable that either hydrogen or carbon monoxide would result from such a reaction as that under consideration, since the former would be liberated in a nascent state very easily oxidized and the latter could be formed only by a decomposition of the oxalate molecule in a way never observed except under the action of a strong dehydrating agent, *e. g.*, concentrated sulfuric acid.

The possibility of the formation of hydrogen peroxide or higher carbon oxides has been discussed by Schroeder.¹ This could lead to error under only the first of the following two conditions, *viz.*, that they subsequently decomposed, setting free oxygen or that they remained intact at the end point. The former condition has already been discussed (p. 412); the latter possibility, that they remain unacted upon to the end of the titration, is both improbable and immaterial, since, when the end-point correction is employed, the excess of oxygen which they might contain would undoubtedly be corrected for by the "blank" as determined with potassium iodide.

2. Summary and Conclusions.

As is indicated in the discussion immediately preceding, there appear to be only two sources of variation from the normal course of the reaction which are at all probable, *viz.*, loss of oxygen from the solution or oxidation of part of the oxalic acid by atmospheric action. Although either of these theories explains a large part of the experimental facts, only the former can be held in the light of the experiments of Tables VII and the other facts discussed in connection with this table.

Therefore, if the main source of error is due to oxygen losses, the higher values obtained in the various series are more nearly correct. This conclusion has been accepted as a working basis for the recommendations regarding choice of conditions for titration. Indeed such choice cannot be far in error, since the greatest discrepancies noted under wide ranges of conditions is not over 0.2% (not including errors due to long standing, inefficient stirring and excessively rapid permanganate addition just at the end-point).

¹ *Z. öffent. Chem.*, 16, 270 (1910).

3. Method of Procedure Recommended.

Although it can be seen that under quite varied conditions of standardization, the values obtained for the permanganate will vary less than one part in a thousand, it seems desirable to fix more definitely the conditions of titration, both in order to make the results obtained slightly more precise and also to ensure the use of those conditions under which the difficulty of proper operation is a minimum. For this purpose the following detailed method of operation is recommended:

In a 400 cc. beaker dissolve 0.25–0.3 g. of sodium oxalate in 200 to 250 cc. of hot water (80 to 90°) and add 10 cc. of (1 : 1) sulfuric acid. Titrate at once with 0.1 N KMnO_4 solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10–15 cc. per minute and the last $\frac{1}{2}$ –1 cc. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The solution should not be below 60° by the time the end-point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos covered hot plate during the titration. The use of a small thermometer as stirring rod is most convenient in these titrations, as the variation of temperature is then easily observed.

4. Accuracy and Precision Attainable.

The agreement of duplicates in the numerous tables given above shows the precision which can be expected in the use of sodium oxalate when the conditions of titration are regulated. It appears that agreement of duplicates to one part in two thousand should be regularly obtained if weight burets are used. Failure to obtain this precision should be at once taken to mean that some condition has not been regulated with sufficient care.

Although the absolute accuracy of the values obtained under different conditions has not yet been studied, it seems probable that if the method recommended is followed the error will not exceed 0.1% and probably will be less than 0.05%.

It is hoped to undertake a comparison of this method with other oxidimetric standards, particularly iron, silver, and iodine, in order to check its value. However, such work involves one uncertainty which renders the best results which could be obtained probably no more conclusive than those now at hand. The difficulty is that of end-points, for in each case mentioned the uncertainty in the blank correction required for an end-point is about of the same order as that of the uncertainty in the oxalate values, namely, 0.1% (usually equivalent to 0.05 cc. of 0.1 N

KMnO₄). We, therefore, at the present time, would assume no greater absolute accuracy for the values obtainable than 0.1%.

The author takes pleasure in acknowledging the kindness of Dr. W. F. Hillebrand in giving valuable advice during the course of the work reported in this article.

BUREAU OF STANDARDS, WASHINGTON, D. C.

THE CARD INDEX TO CHEMICAL LITERATURE OF THE UNITED STATES PATENT OFFICE.

By EDWIN A. HILL.

Received January 9, 1912.

Previous papers, fully describing the system used, have been published in *THIS JOURNAL*, 22, 478 (1900) and 29, 936 (1907), this paper being in the nature of a report of progress, the index now containing about 1,200,000 cards, of which 700,000 are chemical titles and names of substances and 500,000 are formula cards. At the present time a force of four persons is at work in keeping up to date with the bimonthly issues of the Abstracts of the Society, which receive a very minute treatment, some of the half and quarter page abstracts in the Organic section at times giving rise to from 50 to 200 cards each, as every substance named is carded. Our force, however, is not sufficient to do all that has been blocked out as desirable, and some work which we hope to do in the future is now in abeyance for lack of force, *e. g.*:

J. Chem. Soc. (London), from 1907 to date.

Supplements to Richter's "Lexikon der Kohlenstoff Verbindungen."

Remaining volumes of "Beilstein."

Wurtz's "Dictionnaire de Chimie."

Watts' "Dictionary of Chemistry" (4-vol. edition).

And some other works which I will not take time to mention, to say nothing of the large number of chemical patents not yet indexed.

For convenience of reference I append a table showing the work done since 1907 (for previous work see the articles already published), so that any one caring to make use of the index can know exactly what is the field covered, which, including the English abstracts to 1907 and our own to date with the exception of Vols. 1 and 2, which will eventually be included, is fairly complete.

This index, while intended primarily for the use of the office in the granting of chemical patents, is thrown open to the general public without charge, any one being allowed to consult it and make extracts from it without payment of fees, and more than once advanced students of our universities have greatly lightened their labors in the examination of literature in preparing their theses, and its use by patent solicitors and attorneys and chemical engineers in investigating questions of patent-

bility, novelty, and patent validity in connection with chemical inventions is becoming quite frequent, while the assistant examiners of the chemical divisions of the office make constant use of it.

Those wishing to make use of it and unable to come to Washington in person can easily arrange to have any of the numerous men of science in Washington do so for them, or through Prof. C. E. Munroe or Asst. Prof. O. D. Swett, of the George Washington University here, could probably arrange to have such work done for them at moderate charges by some of the chemical students in that university, and again the firm of Longfellow and Bitzer, of 622 F. Street, N. W., this city, is one of several firms of local typewriters and stenographers who make a specialty of making copies and extracts from the various books and records of the Patent Office.

In the table following in the column "How indexed," the legend "Page by page" means an inspection of each page and an indexing of all substances and general titles mentioned; "Index copied" means that the titles in the index are duplicated by typewriter on cards; "Text cut and pasted" means that two copies of the work were obtained and each page cut up into small items and separately pasted upon the cards; "Index cut and pasted" indicates the same treatment of two copies of the index; and "Chem. index copied" means that the chemical portion only of the index was so treated.

PUBLICATIONS INDEXED SINCE 1907.

Title of publication, etc.	How indexed.
<i>American Association for Advancement of Science, Reports, etc., on Chem. Lit.</i> (1884-1898).....	page by page
<i>American Chemical Journal</i> (Easton, Pa.), Vols. 24-36 (1900-1906).....	index copied
<i>American Chemical Society Abstracts</i> , Vols. 3 and 4 (1909-1910).....	text cut and pasted
<i>American Electrochemical Society Journal</i> , Vol. 2 (1902).....	index copied
<i>Beilstein, F.</i> , "Handbook of Organic Chemistry," Vols. I and II.....	index copied
<i>Berichte der deutschen chemischen Gesellschaft</i> , Vols. 31 to 33 (1898-1900).....	index cut and pasted
<i>Census, 12th U. S. Bulletin</i> 201, "Chemicals and Allied Products".....	text cut and pasted
<i>Chemical News</i> (London), 2 Vols. for 1900.....	index copied
<i>Chemical Society</i> (London, Eng.), <i>Collective Index</i> (1873-1882)	text cut and pasted
<i>Chemical Society</i> (London, Eng.), <i>Collective Index</i> (1883-1892)	text cut and pasted
<i>Chemical Society</i> (London, Eng.), <i>Annual Indexes</i> (1893-1907)	text cut and pasted
<i>Clarke, F. W.</i> , "Constitution of the Silicates," <i>Bulletin</i> 125, Geological Survey.....	page by page
<i>Greenwood Guide to Technical and Commercial Books</i> (1904)	chem. index copied
<i>Journal of Physical Chemistry</i> , Vols. 4 and 5 (1900-1901).....	index cut and pasted
<i>Merck, Index for 1907</i>	page by page
<i>Moissan, "Traité de Chemie Minerale,"</i> Vols. I and II (1904-5).....	page by page

PUBLICATIONS INDEXED SINCE 1907 (*continued*).

Title of publication, etc.	How indexed.
<i>Scientific American</i> , "Cyc. of Receipts, etc.," (1892) (Chem. Syn.).....	page by page
<i>Society of Chemical Industry, Collective Index</i> (Vols. 1 to 14) ..	text cut and pasted
<i>Society of Chemical Industry, Vols. 15 to 19</i> (1896-1900).....	index cut and pasted
<i>Strecker, A.</i> , "Textbook of Organic Chemistry" (1882), pp. 789.....	index copied

SOME NEW FORMS OF PROJECTION APPARATUS.

By L. M. DENNIS.

Received December 18, 1911.

The decomposition of water by electrolysis, the union of hydrogen and oxygen to form water, the electrolysis of hydrochloric acid, and other experiments with gases may satisfactorily be demonstrated before small classes by means of the lecture apparatus designed by Hofmann and others. When, however, the audience numbers several hundred, the apparatus is too small to render the details of the experiment clearly visible in all parts of the lecture room.

To obviate this difficulty, the small apparatus illustrated in Figs. 1 to 5 was designed for the projection of such experiments. Since round

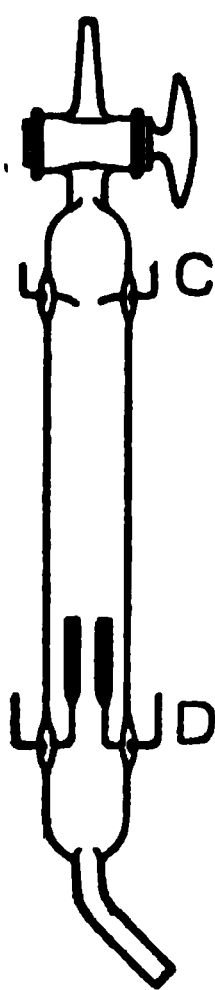


Fig. 1.

glass tubes are not suited to projection before the lantern, those parts of the apparatus that are to be projected upon the screen are made of flattened glass tubes with the sides as nearly parallel as possible. The main tubes of the apparatus shown in Figs. 1, 3 and 4 are 12 mm. wide and 4 mm. thick, while the tube C of Fig. 5 is 28 mm. wide and 14 mm. thick. As the usual diameter of the condensers of lanterns that are used for projection is about 11 cm., the height of that part of the apparatus that is to be projected upon the screen, for example, from the stopcock down to D in Fig. 1, is about 9 cm.

Fig. 1 shows an apparatus designed to illustrate the fact that the gases liberated when water is decomposed by an electric current recombine when the mixture is ignited by an electric spark and leave no gas residue. The tube is connected with the level tube (Fig. 2) by a piece of small rubber tubing about 25 cm. long, is filled with dilute sulfuric acid, and is held in front of the condenser of the lantern by a small clamp that grasps the tube just below the terminals D. The lower terminals are connected with a suitable source of direct current and the terminals at C are

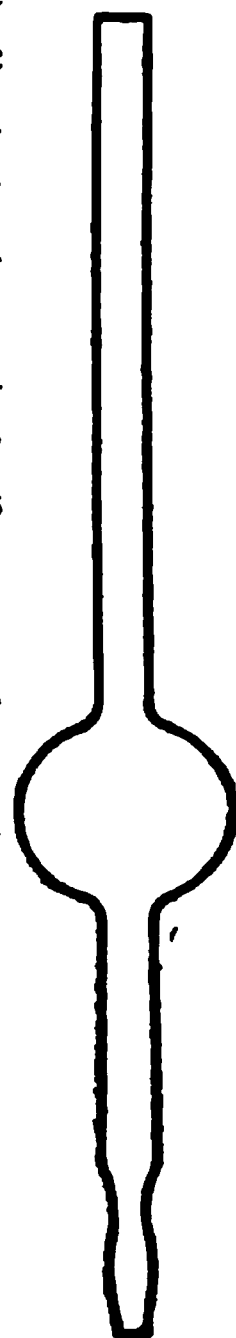


Fig. 2.

joined by light wires to the poles of a small induction coil. The current is then passed across the lower terminals, and when the evolved gas fills

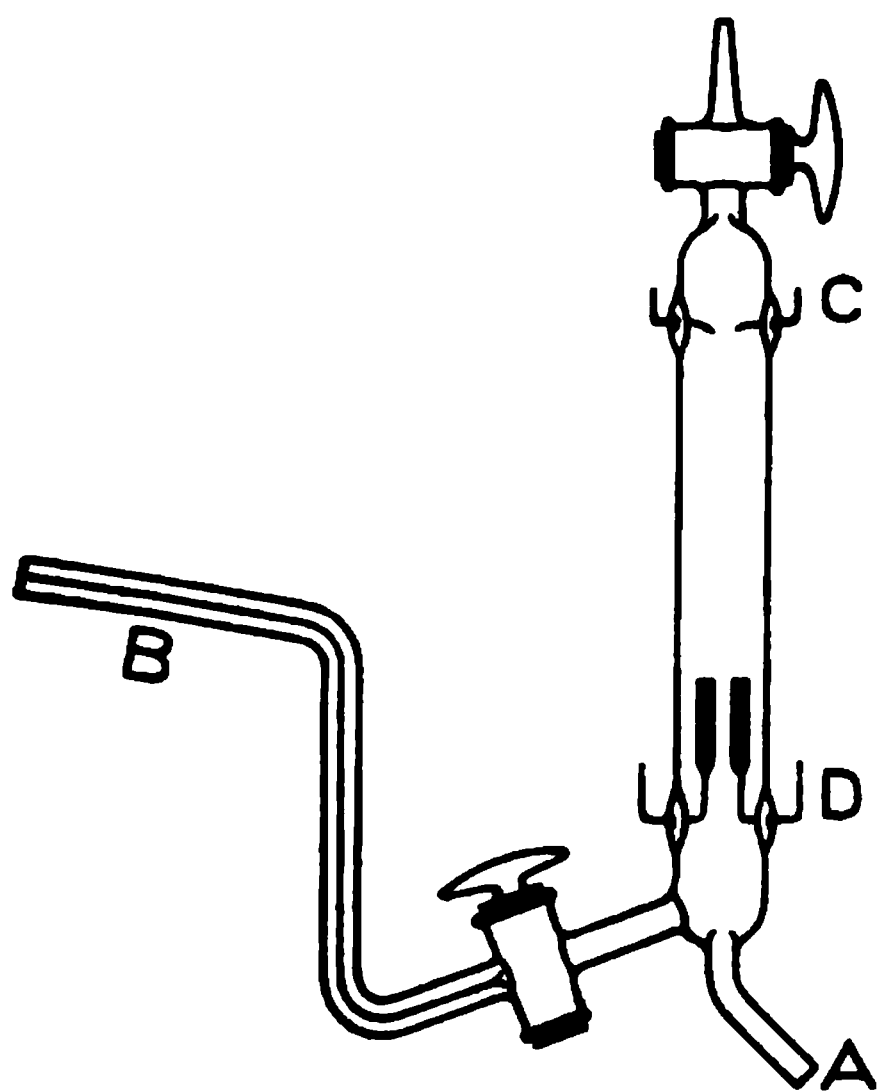


Fig. 3.

the tube down nearly to these terminals the current is shut off. Upon passing a spark between the upper terminals C the hydrogen and oxygen recombine and the confining liquid rises to the stopcock.

To show that a residue of gas remains after the explosion if either the hydrogen or oxygen be present in excess of the amount to which it is liberated when the water is decomposed by electrolysis, the tube shown in Fig. 3 is used. The end A is connected with the level tube as usual, and both the projection tube and the side capillary tube B are filled with dilute sulfuric acid. The end of the tube B is connected with an apparatus

furnishing either hydrogen or oxygen. The current is then allowed to pass across the terminals at D until the tube is about half full of oxyhydrogen gas. The current is shut off, and hydrogen or oxygen is passed through B until the liquid falls to the terminals D. After explosion of the mixture, a volume of gas equal to that of the hydrogen or oxygen added will remain in the tube.

Fig. 4 shows an apparatus that may be used to demonstrate the relative volumes of hydrogen and oxygen that are set free when water is electrolyzed, or the relative volumes of hydrogen and chlorine that are set free when hydrochloric acid is electrolyzed. In the electrolysis of acidulated water, terminals of platinum wire are used; for the decomposition of hydrochloric acid, carbon terminals of the form shown in the illustration are employed. The level tube is here attached to the short side-arm A.

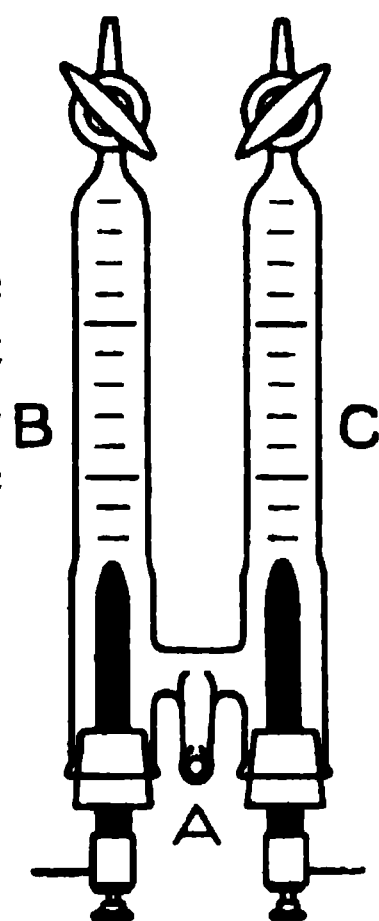


Fig. 4.

Fig. 5 is the decomposition tube of a Hempel nitrometer for showing the formation of nitric oxide when an aqueous solution of sodium nitrate is decomposed by concentrated sulfuric acid in the presence of mercury.

All of the above apparatus may be obtained from Greiner and Friedrichs, Stützerbach, Germany.

In the projection of chemical lecture experiments it is desirable to have the projection apparatus stand upon the lecture table where it may be

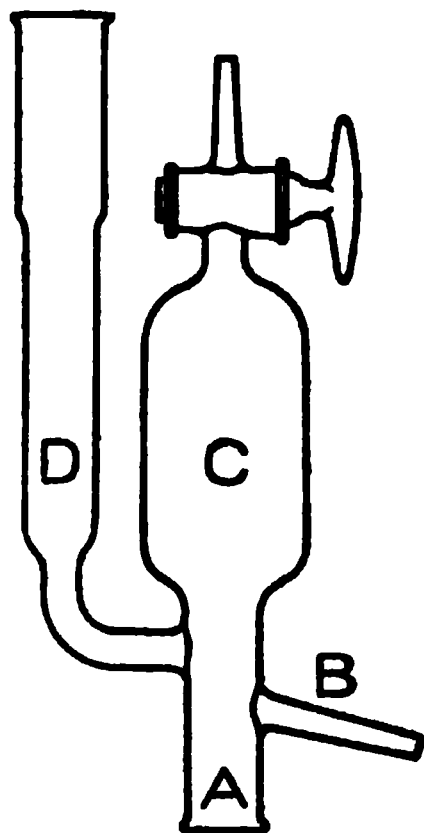


Fig. 5.

manipulated by the lecturer himself. This usually necessitates the projection of the experiment upon a screen placed at the side of the lecture room where the images cannot easily be seen by students sitting close to the wall on that side of the room. By means of the arrangement shown in Fig. 6 the experiments that are to be projected may be performed upon the lecture table itself and the image reflected by the mirror *M* directly back upon the screen *S* behind the lecturer. The mirror *M* is simply a piece of heavy French mirror about 18 cm. square and mounted in a frame. To avoid distortion of the image upon the screen, the screen is mounted on a wooden frame that is hinged at the bottom and that can be set at any desired angle with the back wall by cords that are

fastened to either edge and pass through pulleys on the wall down to the cleats *C*.

It is ordinarily impossible to show to more than a very few students at a time the interesting and instructive experiment of Mayer, described by J. J. Thompson¹ and others, in which small magnetized steel needles, thrust through disks of cork and floated upon water, assume in the magnetic field configurations that vary as the number of needles is changed. An attempt to project the experiment by throwing the light from the lantern up through a glass box containing water and the floating magnets and then reflecting the light upon the screen by a mirror, did not give satisfactory results because the bar magnet had to be placed below the lower

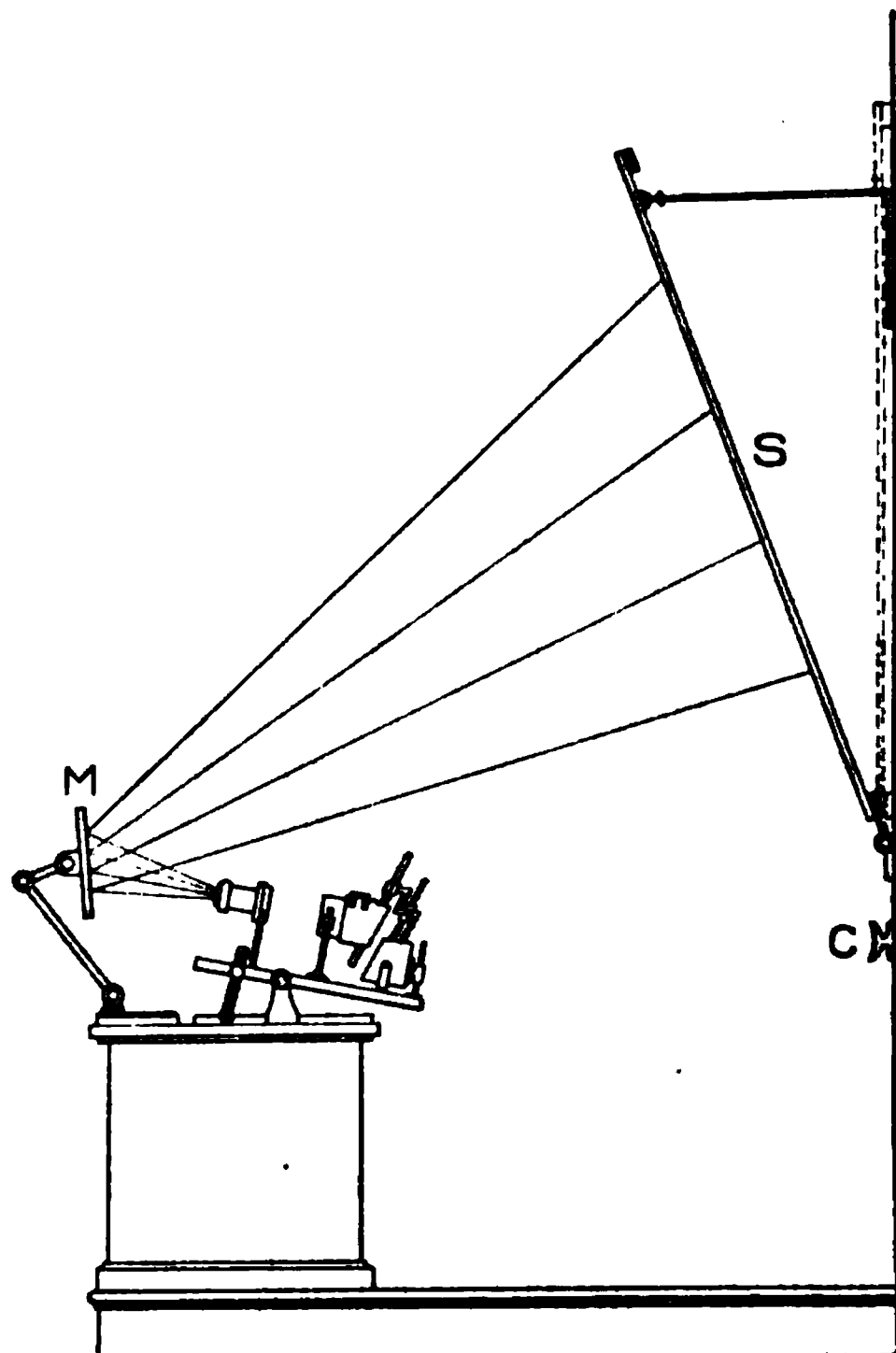


Fig. 6.

¹ "Electricity and Matter," Chapter 5, p. 114.

mirror or above the upper mirror at so considerable a distance from the needles that they did not readily assume the various groupings described by Mayer and did not readily change from one configuration to another. This difficulty has been cleverly overcome by Mr. F. H. Rhodes, of this laboratory, who uses in place of the bar magnet a solenoid fixed in position between the two mirrors as shown in Fig. 7. The light from the lantern is reflected upward by the mirror *M* through the solenoid *S*, the condenser *C*, and a Leybold glass cell *H*, and is then thrown upon the screen by the mirror *N* and the objective *O*. The solenoid consists of three layers of insulated No. 12 copper wire, 30 to 35 turns in each layer, wrapped around a porous cup from which the bottom has been cut off.

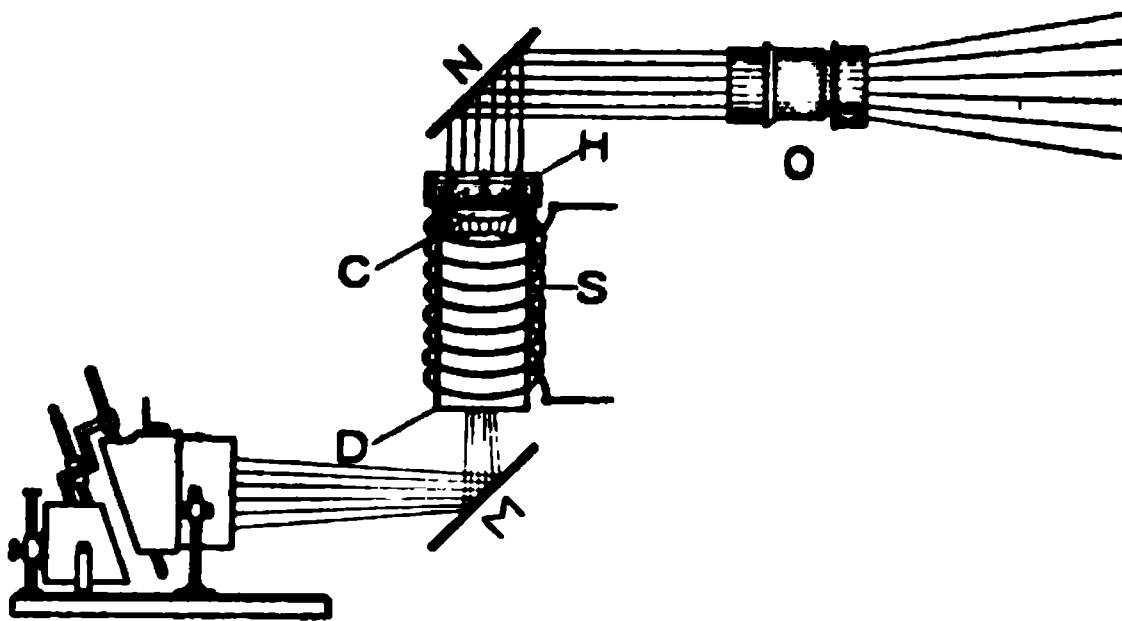


Fig. 7.

The dimensions of the cylinder *D* made from the porous cup are: inner diameter, 8 cm.; outer diameter, 9.5 cm.; and height, 22 cm. The solenoid may be held in place by fastening it in a ring attached to an iron retort stand. Resting upon the upper end of the porous cup is the condenser *C* which in this case was taken from another projecting lantern. The glass cell *H* measures 10 cm. on each side and is 3 cm. deep. It is filled nearly to the top with water and rests upon the face of the condenser *C*. *O* is the objective of the lantern itself.

The needles are ordinary, small, steel sewing needles about 27 mm. long. They were magnetized to as nearly equal strength as possible and were then thrust through thin cork disks about 7 mm. in diameter to such position that about two-thirds of the needle projected below the disk. The needles and corks were then dipped into molten paraffin. A current of from 7 to 8 amperes through the solenoid gives a field of such intensity that the needles when floated upon the water in *H* readily assume position and as readily show change in configuration when the number of needles is varied.

[CONTRIBUTION FROM THE NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION
OF WASHINGTON, BOSTON, MASS.]

THE SOURCES OF ERROR AND THE ELECTROLYTIC STANDARD- IZATION OF THE CONDITIONS OF THE IODIDE METHOD OF COPPER ANALYSIS.

BY AMOS W. PETERS.

Received February 7, 1912.

TABLE OF CONTENTS.—1. Introduction. 2. A Critique of Some Methods of Standardization of Thiosulfate Solutions. 3. A Simple and Rapid Method of Electrolysis of Copper Solutions with a Tartrate-cyanide Electrolyte. 4. A Method for the Preparation of Nitric Acid Solutions of Copper or of its Compounds for the Iodide Method. 5. The Conditions for the Standardization of Thiosulfate Solutions by Means of Copper and of Iodine and the Application of the Iodide Method to Alkaline Tartrate Solutions from Sugar Analyses. 6. Summary of the Conditions of the Iodide Method for the Greatest Accuracy and Sensitivity Especially in the Analysis of Alkaline Tartrate Solutions. 7. Summary of Results.

1. Introduction.

This study of the iodide method had its origin in the necessity for very accurate volumetric determinations of the copper in the alkaline tartrates from sugar analyses. It is a preliminary to an examination and improvement of copper reduction methods of sugar analysis which will soon be published. When the results by the iodide method as at first applied were compared with electrolytic determinations on the same liquids discrepancies occurred which were greater than the supposed limits of error and whose underlying conditions were not understood. Further experiment then showed that the iodide method, even as previously described, could give erroneous results of varying and unknown amount, according to conditions which were accidental and unrecognized by the operator. An examination of the literature also showed that previous experiments were not planned advantageously to show what the liabilities to error are in the general application of the method. The special nature of the conditions under which accurate results were obtained in test analyses or the extent of their significance was only partially recognized. In the present work the point of view differs markedly in that the methods and conditions to be tested are regarded as procedures for obtaining the standard value of the thiosulfate solution which measures values in the iodide method. The other point of view by which a standard value obtained under certain conditions is accepted and then is inadvertently applied to any thiosulfate readings obscures the real sensitiveness of the iodide method to change of conditions. This leads to a false confidence in the results which is enhanced by the supposed electrolytic control. To this criticism it might be replied that an analysis should be made only under those conditions under which the standardization was made. To what extent this is feasible in view of the stand-

ard conditions which must be duplicated and in view of the conditions presented by unknown copper solutions to be estimated, will appear when the results of the experiments here presented have been considered. These observations seem to lead rather to the contrary very empirical and inconvenient but logical proposal that standardizations be made under those conditions under which the copper in each specific case is to be measured. This would lead to a multiplicity of standard values, and it was considered more advisable to determine how one fundamental standard value could be used by the adjustment of the conditions or by the quantitative compensation of the errors due to variable conditions.

The standards of accuracy adopted may be described as follows: It is assumed that in general such well developed methods of standardization, *e. g.*, as that of iodine for thiosulfate, readily permits of renewed standardization, certainly to within 0.1%, each standardization including not fewer than four concordant titrations. From this it follows that when the average values found by two different methods differ by more than the deviations of the individual titrations from their respective mean then some other factor than that of the unavoidable accidental errors of measurement is involved. In the present work there will be found sufficient duplication of values to enable the reader to determine by inspection whether the differences between the frequently occurring averages found in the tables are large enough to be significant. This is a very important criterion, for whether a difference is to be regarded as large or small primarily depends upon the sensitiveness of the method.

2. A Critique of Some Methods of Standardization of Thiosulfate Solutions.

From the standpoint of economy of time in making numerous estimations of copper a volumetric method must take precedence over any known gravimetric process. The iodide method of de Haën,¹ as subsequently developed by numerous analysts, gives, when certain conditions are observed, very accurate results with small expenditure of time. In this method the iodine which is liberated in equivalent amount from potassium iodide is estimated by a standardized sodium thiosulfate solution. The iodide method is properly controlled, as will be shown, by means of a standard copper solution whose value has been determined either by electrolytic deposition from a given volume or by weighing metallic copper of known purity and dissolving it to volume under certain conditions made necessary by the iodide method. In other words, the standardization of thiosulfate to be used for the measurement of copper can be correctly made only by means of standard copper or by other methods, if any, which give the same copper value for the thiosulfate. Now some other methods in common use for standardizing the

¹ *Ann.*, 91, 237 (1854).

thiosulfate do not give the same value as copper would, so that the actual copper value of a thiosulfate solution is not indicated by its normality, if the latter has been obtained by means of, *e. g.*, a standard iodine or a standard dichromate solution.

Thus Bray and MacKay¹ observed a discrepancy of over 0.2% between the standard values of the same thiosulfate solution as found by standard potassium iodide and by electrolytically controlled copper. They state (p. 1199) that "the conclusion was finally reached that the absolute accuracy of the copper standard is not quite so high as we had at first supposed." I have also standardized a thiosulfate solution by the iodide method of Bray and MacKay and have likewise obtained results discrepant with the copper standard. Bray and MacKay suggest that the failure of the copper standardization to agree with that by iodine may be due to adsorption or solution of some iodine by the precipitated cuprous iodide with the result of too low a titration value for the thiosulfate. These authors justly regard the method of standardization by means of iodine as the one of highest absolute accuracy. Bray and MacKay (p. 1198) also standardized thiosulfate by means of potassium permanganate (which in turn had been standardized against sodium oxalate) and observed a discrepancy of at least 0.15 to 0.20% compared with the iodine method. The value obtained for the thiosulfate by the copper method was greater, and that by the permanganate method was lower, than the value by iodine. All these methods gave results concordant with themselves and their variations from each other exceed the limits of accidental error.

An illuminating comparison of the results by different substances that have been proposed and in some cases extensively used for the purpose of iodometric standardization is due to Julius Wagner.² He standardized thiosulfate solutions by means of potassium dichromate, potassium biniodate, potassium iodate, sodium iodate, potassium bromate, sodium bromate, and he also determined the conditions for the testing and purification of these substances. None of the other results could be made to agree with the dichromate standard, and the latter was found in error on account of the catalytic action of chromic acid on the liberation of iodine from potassium iodide. The conclusions of Wagner as they bear on the selection of a standardization of thiosulfate for absolute accuracy may be shown by brief quotations from the article cited as follows: p. 427: "Die Titerstellung der jodometrischen Lösungen gründet sich jetztwohl allgemein auf die Erzeugung von Jod in angesäuerter Jodkaliumlösung." p. 451: "Praktisch ergibt sich der Schluss das man Kaliumbichromat als Mittel zur jodometrischen Titerstellung verwerfen muss.

¹ THIS JOURNAL, 32, 1193-1204 (1910).

² Z. anorg. Chem., 19, 427-453 (1899).

Allenfalls kann es zu Vergleichszwecken benutzt werden. Am meisten Empfehlung verdient das Kaliumbiodat und demnächst das Kaliumbromat, weil sie sich am leichtesten reinigen lassen." As to the magnitude of limits of error, p. 453: "Alle vorstehenden Titerstellungen und Vergleiche sind innerhalb einer Fehlergrenze von 1% bei mindestens drei Bestimmungen auszuführen." Thus the only standardizations of thiosulfate for absolute accuracy are those which give the same value as pure iodine would, and from the practical standpoint the iodine is best obtained from acidified solutions of iodides and iodates. I have made sufficiently numerous determinations which show that there is not agreement within limits of error between the iodide, biniodate, and iodate standards regarded as one group and the dichromate and pure copper standards as two other groups. The values within the first group were concordant. The question thus arises: What standardization of thiosulfate shall be used when copper is to be estimated by the iodide method? Evidently for this purpose only the empirical value of the thiosulfate as determined by copper of known purity can be used. This principle was not recognized by Gooch and Heath¹ in their examination of the iodide method, in which they controlled their copper solutions electrolytically but apparently standardized their thiosulfate according to the customary systematic normalities.

The facts above described lead to important conclusions regarding the accuracy of copper analyses which are especially significant when gravimetric and volumetric determinations are compared or used interchangeably. In sugar analysis by copper reduction methods the choice of gravimetric or volumetric determination almost always lies open, and these two procedures are assumed to give the same result in terms of copper. Thus, in the "Official and Provisional Methods of Analysis of the Association of Official Agricultural Chemists,"² pp. 51-53, are described six methods for the determination of reduced copper whose results are to be concordant and among these are a volumetric (permanganate) and electrolytic methods. Here again appears, p. 53, the discrepancy between the empirically determined copper value of a standard solution (here permanganate) and that calculated from its systematic normality.

E. Pflüger,³ p. 436, in testing the sulfocyanide method for the volumetric estimation of copper, in this case also found a similar discrepancy and showed that if the atomic weight of copper was taken as 63.47 instead of 63.18, as used by him, the discrepancy would disappear. In the method of Pflüger-Allihn,⁴ as described by Neubauer-Hup-

¹ *Am. J. Sci.*, 24, 65-74 (1907).

² U. S. Dept. of Agriculture, Bur. of Chem., *Bull.* 107 (1907).

³ *Arch. ges. Phys.*, 69, 399-471 (1898).

⁴ *Loc. cit.*

pert,¹ pp. 411-412, volumetric methods (iodide of de Haën and sulfocyanide of Volhard) are even used as controls for the gravimetric process when the precipitated copper may be contaminated. Finally the tabular values of the numerous published methods of sugar analysis by copper reduction are expressed quantitatively in terms of copper. The importance of proving the accuracy of any proposed method for volumetric copper determinations is hence evident. The necessity is still greater when a judgment is to be formed of the accuracy of any given tabular values by means of controls with pure sugar solutions. On account of the previously described discrepancies between different standardizations, this accuracy is attainable volumetrically only by the use of solutions whose value in copper has been obtained empirically and not calculated from their systematic normality or equivalence. The cause of this discrepancy affecting the equivalent value of copper solutions has never been satisfactorily determined. With the use of the modern atomic weight of Cu = 63.57 the discrepancy with the iodide method remains and the proposed theory of the absorption of iodine in this method has also been found untenable (see pp. 446-7). These facts have been emphasized here since accurate volumetric copper determination was adopted as the critical instrument of investigation for the problem of sugar analysis.

3. A Simple and Rapid Method of Electrolysis of Copper Solutions with a Tartrate Cyanide Electrolyte.

A method of electrolysis incidentally developed in connection with this work has the advantage of using the simplest of means and yielding results with a very moderate expenditure of time. It does not compete with the use of rotating electrodes but its simple appliances and satisfactory results may make it useful in those cases where special apparatus is not at hand and particularly for purposes of control in sugar analysis. No effort has been made to effect electrochemical separations by this procedure but simply to determine copper. In view of the fact that the preparation of solutions of copper for the application of the iodide method is always more or less circumstantial a very simple but effective method for this purpose will also be described. As the criticisms of conditions for the iodide method are dependent on the results of electrolysis, the latter process will be described first.

The special characteristics of this procedure for electrolysis are primarily (a) the composition of the electrolyte used and consequently (b) the comparatively high voltage and current density compatible with good deposits which this electrolyte permits, and (c) the rapid and continuous mixture of the liquid by both the evolution of gas and the external application of heat even to boiling. The attempt to electrolyze the alkaline

¹ Neubauer-Huppert, "Analyse des Harns," Wiesbaden, 1910.

tartrate solutions of copper from sugar analyses led to the observation that tartrates and citrates in either alkaline or citric acid solution are media in which the electric current deposits copper very rapidly. The observations made on a considerable number of other organic substances will not be reported. The character of the deposit, however, is not good from an analytical standpoint, exhibiting the sponginess, loose adherence, and sometimes carbonaceous appearance which are familiar difficulties in electrodeposition. No use could be made of this rapid rate of deposition until it was discovered that the addition of potassium cyanide in small amount was a means of completely controlling the character of the deposit. A dull metallic or bright copper color could be produced according to the amount of cyanide under the same current density and the deposit varied likewise from sufficient adherence for all necessary washing and handling to a hard coating that could not be rubbed off with the finger, even with pressure. It was observed, however, that alkaline cyanide had a solvent action upon the deposit and thus a retarding effect antagonistic to that of the tartrate and citrate. This influence made itself especially felt in the effort to deposit the final, small portions of the copper from a solution. The conditions here are exactly analogous to those with nitric acid in the customary sulfuric-nitric electrolytes. In the present method a peculiar use is made of cyanide in that its quantity is definitely limited to the least amount that will give a satisfactory hardness and color of deposit under a given set of conditions. The amount of cyanide used is always less than is required to decolorize the copper solution. The composition and use of the electrolyte finally adopted was as follows: An alkaline tartrate mixture is made containing in a final volume of 100 cc. 35 grams of pure sodium potassium tartrate (Rochelle salt) and 25 grams of potassium hydroxide, purified by alcohol. This is almost exactly the composition of Allihn's alkaline tartrate solution, which may also be used. Customarily a volume of 10 cc. of the copper solution, which may be slightly acid or alkaline, is placed in either the platinum dish or the glass beaker in which the electrolysis is to be made. An approximately equal volume of the alkaline tartrate solution is then added, but as much as two volumes may be used to one of the copper solution, especially when the latter contains some acid, which may be sulfuric or nitric. For larger volumes of electrolyte as for filling a test tube used as cathode vessel the rule is observed that one-half or more of the total volume should consist of the alkaline tartrate solution. In this connection it should be stated that when the alkaline tartrate has deteriorated by much exposure to the air it will cause much trouble by excessive foaming. A saturated aqueous solution of potassium cyanide is then added in quantities ranging from 0.4 to 1.0 cc. or more, depending upon the absolute amount of copper and

regulated by the character of the deposit. If the deposit is too soft or dark colored under a given set of conditions more cyanide is used, but it must be remembered that too much cyanide will lengthen the time required for complete deposition.

The anode in all cases is either a flat or a cylindrical spiral of platinum wire for use with a platinum dish or a narrow beaker, respectively. *Its distance from the cathode surface should be one centimeter or less.* For cathode a platinum dish may be used, which is set on a piece of sheet brass to which the cathode connection is made. The brass is more easily kept clean than copper sheet, as it oxidizes less in the air. This support for the cathode of platinum or for a glass beaker is used so that the electrolyte can be heated by a small Bunsen flame beneath and to one side of the vessel. The sheet metal is carried by a ring stand and the same stand by means of a clamp carries the anode coil. The anode is the only platinum necessary as a copper cathode will also give accurate results as will be shown subsequently. Sheet copper is cut in oblong form with a long, narrow strip extending at one end and at right angles to the length of the wider portion of the piece. This is coiled into the form of a cylinder and with its circumference not quite closed it is then placed in a narrow beaker of twice the height of the cylinder. The narrow strip is bent at right angles over the edge of the beaker for connection with the cathodic pole. The beaker here used had a capacity of 50 cc., a diameter of 3.5 cm., and a height of 7.0 cm. The height of the cylinder should be such that the volume of electrolyte to be used is sufficient to immerse it completely, except the extending strip. To secure large cathode surface with nearness of electrodes a long and wide test tube, *e. g.*, 20 × 2.5 cm. or larger, is substituted for the narrow beaker and the copper cathode is cut to this size as above described. The copper cathode should be cleaned with nitric acid followed by water, washed in alcohol and ether, dried while held by the hand over a source of heat, completely air-cooled and then weighed. The amount of copper deposited on such an electrode is, of course, found by taking the difference between the initial and final weight for each determination. The initial weight will vary after each preparation of the electrode by cleaning with nitric acid, washing and drying. It was, however, necessary to test whether the copper electrode will remain of constant weight like a platinum cathode through the process of preparation, omitting the acid treatment but including washing, drying, exposure to air, etc., by which, at the close of electrolysis, it must be prepared for weighing. Repetitions of this procedure gave the following results:

After first preparation = 17.7801 grams. After second preparation = 17.7799 grams. After third preparation = 17.7801 grams. After fourth preparation including standing in alcohol for 5 minutes = 17.7801 grams. After standing on balance pan for 1 hour = 17.7802 grams. After fifth preparation = 17.7801 grams.

These results are sufficient to show the constancy of the copper cathode. The principal conditions for accuracy are that it be freshly cleaned immediately before use (even in immediately succeeding electrolyses), that it be thoroughly air-cooled before weighing, and that it be handled with the fingers only at the edge of the extending strip. The same cathode may be used many times, but it should be weighed each time immediately before and immediately after use. If unused for some time it should be freshly cleaned, washed, heated and air-dried before renewed use. These precautions are important for accurate results with the copper cathode, but have less significance with platinum.

In all cases the anode wire must extend well out of the platinum dish or the glass beaker so that these vessels can be covered with split watch glasses to prevent loss by spraying. The ring stand carrying the whole apparatus is best set in or near a sink so that at the close of the electrolysis the current can be interrupted by running a stream of water from a rubber tubing attached to the tap into the cathode vessel until the illumination of the resistance lamp completely disappears. By this method no solution of copper can occur. The cathode is then prepared for weighing as before described, avoiding any heat greater than that of warmth to the hand.

Among the various factors upon which the rate of electrodeposition depends it is well known that one of the most important is the rapid change of fresh portions of electrolyte upon the surface of the electrodes. In the present method this change is made continuous and rapid both by an abundant evolution of gas and by the continuous application of heat from a small Bunsen burner, placed under the brass plate and at some distance to one side of the position of the cathode vessel. With the test tube arrangement a wire gauze is interposed between the test tube and a small Bunsen flame beneath. As previously explained, the total volume of mixed electrolyte which was customarily used was about 25 cc. with the platinum dish or the beaker and 70 cc. with the test tube. The capacity of the platinum evaporating dish used as cathode was about 40 cc. and its dimensions were approximately 50 mm. in diameter and 25 mm. in depth. The 25 cc. of electrolyte covered a platinum surface of approximately 40 sq. cm. The copper electrode used for the beaker was approximately 10 cm. long and 2.7 cm. wide. Three triangular notches were cut out of its lower edge to facilitate the passage of liquid, as the copper cylinder stood on the bottom of the glass beaker. The total area of this copper cathode was approximately 50 sq. cm. The test tube cathode of copper measured 15×6 cm. when flat.

The direct 110 volt current, the same as that of the lighting system, was used, with the ordinary lamp resistance in circuit. A resistance of three thirty-two candle-power lamps in parallel was customarily inter-

posed in the circuit. The amount of current was sufficient to heat the electrolyte and to give rise to an abundant evolution of gas, by means of which the liquid was kept well mixed. When the three thirty-two candle-power lamps and the electrolyte as above described were in circuit the voltage measured 2.6 and the amperage 2.85. Thus the density ND_{100} for the platinum cathode was 1.14.

To test for the completion of the deposition a modification of the exceedingly delicate hydrobromic acid test for cupric copper of Endemann and Prochazka¹ was used. One volume of concentrated sulfuric acid is diluted with two to three volumes of distilled water. About 1 cc. of this diluted acid is placed in a narrow test tube, a few crystals of potassium bromide are added and the whole is heated to boiling. If to the hot mixture one drop of a solution containing as little as 0.007 mg. of copper is added, a red color will develop. The color is best seen by placing the test tube in the hollow of a white porcelain evaporating dish held by the observer on a level with his eye while his back is turned toward the source of daylight. One or two drops of the alkalin electrolyte here used when added to the above hot hydrobromic acid mixture will at once become acidified and show the presence of a very small amount of copper. The electrolyte loses its blue color as the electrodeposition proceeds and the test for copper should not be made until some time after the liquid has lost its blue color.

By the above method repeated determinations have been made on the same solution of pure copper sulfate delivered in approximately 10 cc. volumes by an automatic pipet of constant delivery as shown by weighing repeated deliveries as in calibration. The results were often identical but differed at most by only one or sometimes two-tenths of a milligram of copper on a total of about 177 milligrams. This amount was fully deposited in less than thirty minutes with the platinum dish and beaker cathodes and in less than fifteen minutes with the test tube arrangement. On account of the similarity of composition of the electrolyte and of the alkalin copper solutions much used for sugar analysis this method is well adapted for the accurate control of these methods by the determination of copper.

4. A Method for the Preparation of Nitric Acid Solutions of Copper or of Its Compounds for the Iodide Method.

As nitric acid is the most available acid for the solution of copper and of its compounds for analytical purposes, much attention has been given to methods for the removal of the lower oxides of nitrogen in preparation for the iodide method. Evaporation with sulfuric acid nearly to dryness and to the evolution of white fumes is a well known but inconvenient method. The preparation of the nitric acid solution by boiling,

¹ Endemann and Prochazka, *Chem. News*, 42, 8 (1880).

followed by a treatment with ammonia, then heating again and then adding acetic acid and again boiling, as described by Low,¹ pp. 84-85, is most frequently used. In former editions Low² included a treatment with bromine in the procedure just described "to insure complete destruction or removal of the red fumes." The last boiling (with acetic acid, etc.) he emphasizes as important "as it effects the neutralization or expulsion of any remaining oxidizing compounds that would cause a return of the blue color after titration." A method that avoids boiling is due to Kendall,³ sodium hypochlorite and phenol with subsequent neutralization being used. The very simple method here proposed which serves in the determination of unknown copper also consists in vigorously boiling the nitric acid solution of copper for 5-10 minutes with a little pure talcum powder in the presence or the absence of sulfuric acid. It was observed that a sulfuric-nitric acid solution of metallic copper, which had been freed from brown fumes by boiling, evolved an additional quantity of brown fumes upon the addition of powdered talcum to the hot liquid. The vigorous ebullition which occurs under these conditions greatly accelerates the removal of lower oxides of nitrogen, including nitrous acid. No bumping or spurting occurs. The copper or its compound is dissolved in an Erlenmeyer flask in the least required volume of concentrated nitric acid, to which one-half its volume of water has been added. Five to 10 cc. of this diluted acid should be used for 0.5 g. or less of copper. After solution with the free use of heat until brown fumes are no longer apparent to the eye 15 to 25 cc. of distilled water and a little pure powdered talcum are added. The mixture is then kept in vigorous ebullition for five to ten minutes. The escaping vapors, when not too strongly acid, may be tested for nitrous acid with moist starch-iodide filter paper and the result of this test speedily becomes negative. Ebullition under these conditions is so effective that in preparations for the iodide method evaporation need not be continued to dryness. After cooling, enough distilled water is added to make the volume here required, including reagents, about 120 cc. at the end of titration (see pp. 442-6). In general, a smaller volume would be desirable.

This method has been subjected to numerous tests, of which the following show its accuracy. If the method is accurate, then its simplicity gives it an advantage over all other methods. In one experiment a sample of the purest obtainable metallic copper foil was used. 1.2499 grams were weighed and treated by the nitric acid-talcum procedure, as above described, by adapting the amounts of reagents to this weight of copper.

¹ Low, A. A., "Technical Methods of Ore Analysis," 5th Ed., New York, 1911.

² *Ibid.*, 1st Ed., 1905.

³ THIS JOURNAL, 33, 1947-1952 (1911).

The solution was then made to a volume of 100 cc. and placed in a calibrated buret. Electrolysis by the method previously described gave for two determinations on 10 cc. each, 125.0 and 125.0 mg. of copper. Three titrations of this same solution of 10 cc. each were made by the iodide method as subsequently described by means of a thiosulfate solution, whose standard copper value was to be determined in this way. The thiosulfate volumes thus found were 9.85, 9.85, and 9.87 cc., *i. e.*, an average of 9.86 cc. Hence, $\frac{0.12499}{9.86} = 12.676$ mg. Cu. per cc. of thio-

sulfate. To test the consistency of the method two independent titrations on amounts of copper appropriate for one titration each were made with the same thiosulfate. Weights of copper of 0.3268 and 0.3252 g. required 25.76 and 25.63 cc. of thiosulfate. These titrations gave standard values of the thiosulfate as 12.686 and 12.688 mg. Cu per cc., respectively, which is good agreement with the previous results. The same thiosulfate was now standardized by means of Kahlbaum's purest analyzed copper sulfate of the brand "Zur Analyse mit Garantieschein" described as containing in 10 grams 0.75 mg. of iron oxide and 1.50 mg. of alkali salts, etc., and *no* other metals. An aqueous solution was made in the proportions required for Fehling's solution and placed in a calibrated buret. Electrolysis on two samples of 10 cc. each by the method previously described gave 175.6 and 175.6 mg. of copper. Two titrations by the iodide method were made as subsequently described on 20 cc. each of this copper solution, requiring 27.71 and 27.70 cc., respectively, of the above thiosulfate solution. These values give $\frac{175.6 \times 2}{27.71} =$

12.674 and $\frac{175.6 \times 2}{27.70} = 12.679$ mg. Cu per cc. of thiosulfate. These

values obtained on pure copper sulfate without the nitric acid-talcum procedure compare well with the above values obtained by means of that procedure. This procedure was now applied to two 20 cc. portions of this same copper sulfate solution by the addition of nitric acid containing nitrous acid for the purpose of determining whether the process itself would leave the above values unaltered. The titration results were again 27.71 and 27.70 cc. From all these results it follows that the nitric acid-talcum procedure effectively removes all the decomposition products of nitric acid that would interfere with the accuracy of the iodide method. It was now shown that the method of Low, involving the additional use of ammonia and acetic acid, gave no different results than the above when applied to the same metallic copper, copper sulfate, and thiosulfate. By the metallic copper the standard value of the thiosulfate was found by Low's method as 12.699, 12.679 and 12.700 mg. of Cu per cc., *i. e.*, an average of 12.693. On the copper sulfate solution the titra-

tion results with Low's method were 27.72, 27.71, 27.70 cc. of thiosulfate, i. e., an average of 27.71, which gives $\frac{175.6 \times 2}{27.71} = 12.674$ mg. Cu per cc. of thiosulfate. The average of all the results by Low's method is 12.683 and that by the nitric acid-talcum method is 12.681.

In view of the above comparisons of results the following criticisms appear to be justified. The efficiency of both of these methods is due to the same cause, which is simply the boiling process. In other words, the ammonia and acetic acid treatments in the Low method are superfluous for the purpose of removing nitrous acid, although they may facilitate evaporation by boiling. It may be noted here that Low has now found it feasible to omit the bromine formerly constituting an additional reagent of this method. The reasons given by Low for the use of these reagents have been quoted above.

The method of Kendall¹ is more complicated than either of the methods above discussed and involves the accumulation of salts in the titration liquid. As is shown subsequently in this paper, the results by the iodide method under these conditions may easily deviate from the highest standard of accuracy (see pp. 434, 438). The plan of the test analyses of Kendall would not result in positive evidence on this question. Whether the concentration of the salts by this method is sufficient to affect the results was not tested but seems worthy of consideration, in view of the other data here developed.

5. The Conditions for the Standardization of Thiosulfate Solutions by means of Copper and of Iodine and the Application of the Iodide Method to Alkaline Tartrate Solutions from Sugar Analyses.

(1) *Introduction.*—The most accurate of all methods for the estimation of copper is admittedly the electrolytic. For accuracy, with the advantages of simplicity and speed, no other method is as good as the iodide. The extensive use of the latter method for both scientific and technical purposes gives value to any additional determination of its conditions of accuracy. Owing to the fact that this method depends upon the following well known equilibrium reaction, $2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$, it seems necessary to judge from this standpoint the application of the method to any concrete case. Whether the results obtained by the iodide method represent the copper with quantitative accuracy depends wholly upon the observance of conditions which are somewhat narrowly defined for concrete cases. This circumstance explains why the history of the method shows authoritative analysts among both its advocates and its opponents. These conditions, except certain details that need emphasis, have been much studied, so that further investigation is in danger of dealing with repetitions. Therefore the substance

¹ *Loc. cit.*

of the propositions here to be demonstrated will be at once stated as follows:

A. There is an irreconcilable difference with the use of well known methods between the standard values of a thiosulfate solution as determined by standard iodine (*e. g.*, from potassium iodate, etc.) and by means of pure copper. This difference, when at a minimum, is several times as great as the limits of error of each method of standardization by itself. For accurate copper determination the copper standardization alone can be used and this only when determined under proved conditions.

B. The necessity under the conditions of most frequent occurrence for a definitely regulated concentration of acid in order to attain the highest accuracy and consistency with the iodide method will be shown. This condition has not been sufficiently recognized by some investigators of the method and has been denied by others. For the frequently occurring practical cases where acids and salts are present, which latter depress the ionization of the acid, the influence of this condition becomes of critical importance. This is especially the case in the determination of copper in the filtrates from such analytical processes as sugar reduction methods. The influence of salts on the reaction by which iodine is developed has not been heretofore recognized.

C. The equilibrium reaction above given, upon which the iodide method depends, is much influenced by changes of temperature so that perceptibly more free iodine will be developed at 30° than at 15°. Since, for reasons of expediency, sulfuric acid more or less concentrated is used, this error, designated as the "temperature error," may easily occur on account of insufficient or of excessive cooling. Recognition of this source of error leads to its easy prevention and the details of experiments made on this point will therefore not be presented.

D. The opinion of many, *e. g.*, Kendall,¹ p. 1949, that this equilibrium reaction runs to completion only in small volumes and that consequently small volumes for titration are necessary for accurate results with the iodide method is erroneous. The logically related statement of Moser,² p. 597 and others, that the results of the iodide method are influenced by the concentration of the copper in the titration liquid is also erroneous. For our present knowledge of other factors the experiments of Moser³ p. 598, are inconclusive. It will be shown that the iodide method is exceedingly accurate with quite large as well as quite small amounts of copper, provided its conditions are regulated. The estimations of larger and smaller amounts are strictly proportional even when titrated in the same volume.

¹ THIS JOURNAL, 33, 1947-1952 (1911)

² Z. anal. Chem., 43, 597-608 (1904).

³ Loc. cit.

E. The theory was suggested by Bray and MacKay,¹ p. 1199, that the discrepancy between iodide and copper standardizations described above under A is due to absorption of iodine by solid cuprous iodide. Meidinger and Carl Mohr² showed the possibility of such absorption. Since the absorption might vary under different conditions of dilution, etc., its occurrence has been regarded as a source of error. The theory of absorption as a source of error or as an explanation of the discrepancy of standards is not tenable. This will be shown by determinations in which the cuprous iodide enters wholly into solution before titration.

F. The iodide method is a procedure of empirical character from the standpoint of its conditions of accuracy. The easy variability of its results by acids, salts, temperature, and by the application of the same standard value of thiosulfate to different conditions of titration are not recognized in practice. In these experiments it will be shown how these factors can be either adjusted to accuracy or can be quantitatively compensated.

(2) *The Standard Copper Solution and its Measurement.*—A critical estimation of any given procedure for the iodide method is best obtained by attempting to standardize the thiosulfate by the same procedure and by comparing the quantitative results of different procedures and of different methods of standardization. All the conditions necessary for subsequent analyses may thus be determined.

Standard copper solutions which were to be used for the determination of conditions for the iodide method were prepared by two different procedures, which gave the same quantitative results. The first and preferred method consisted in dissolving the purest crystallized copper sulfate obtainable to an approximately known concentration. The exact concentration of the element copper cannot be calculated with reliability by the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Numerous experiences in making Fehling's copper sulfate solution from the purest as well as the commercial salt led to this conclusion. The results were always low to the extent of a considerable fraction of 1%, even when the salt was pulverized and well air-dried on filter paper. Drying by other means is not permissible. Thus a solution made from the purest obtainable crystallized copper sulfate, which was specially prepared for analytical purposes, when pulverized, air-dried, weighed and made into solution and electrolyzed, was found to contain 0.51% less than the calculated amount of metallic copper. The low result was due presumably to persistently adherent moisture. The standard value of the solutions of pure copper sulfate here used was therefore determined electrolytically as previously described. The second method consisted in the solution by nitric acid

¹ THIS JOURNAL, 32, 1193-1204 (1910).

² Mohr-Classen, "Titrimethode," 7 Aufl., S. 350 (1896).

and by the procedure previously described of the purest metallic copper obtainable and then making a control determination of copper by electrolysis.

For obtaining known quantities of copper there was used a constant volume of copper solution taken from an automatic pipet of approximately 10 cc. delivery. This and other pipets of the same construction were obtained from Bleckmann & Burger, Berlin, and were described as "genau justirt." The exact volume delivered was not of consequence for the present purpose, but its reliability for delivering a constant volume of copper solution was very important. The use of this apparatus was found highly advantageous from both standpoints of accuracy and of economy of time. Its constancy had been tested at various times with very satisfactory results by weighing the quantity of liquid delivered. Two successive deliveries of the stock solution of copper sulfate used below weighed, respectively, 9.4123 and 9.4124 grams.

The reservoir of this pipet contained about one liter of solution and a thermometer was kept in the liquid showing a temperature of 25° when the above deliveries were made. Two successive electrolytic determinations made with the tartrate-cyanide electrolyte on a platinum dish cathode gave 176.9 mg. and 176.9 mg., respectively, of copper. No copper determinable by the hydrobromic acid test remained in solution. For the following experiments we have hence relied upon the pipet to deliver 176.9 mg. of copper so long as the temperature of the liquid remained constant. The ten liters of stock solution from which the automatic pipet was periodically filled was regarded as the standardized copper solution. It was made from the purest purchasable, guaranteed and analyzed copper sulfate, dissolved in pure distilled water.

(3) *The Standardization of Thiosulfate by Iodine from Potassium Iodate.*—For the iodometric standardization of thiosulfate there is here selected, in accordance with preceding discussion (pp. 423–5) of this subject, one of the methods in which iodine is liberated from an acidified solution of iodide and iodate. Repeated determinations made in an earlier stage of this work gave concordant results with the methods that use (a) resublimed iodine, (b) pure potassium iodide and iodate in acetic acid solution, (c) the iodide method of Bray and MacKay.¹ I abstained from the use of biniodate upon finding that the determined acidity of a supposed pure specimen was discrepant with that which is calculated from its formula, $\text{KIO}_3 \cdot \text{HIO}_3$.² The standardizations described below were made by the use of potassium iodide and iodate in acetic acid solution. For the purpose of comparison with the conditions of copper stand-

¹ *Loc. cit.*

² Krauch, C., "The Testing of Chemical Reagents for Purity," 3rd Ed., New York, 1902. See p. 219.

ardization some results obtained with sulfuric acid are also given. Potassium iodate, Merck's Blue Label Reagent and Kahlbaum's purest potassium iodide were used. Their degree of purity and fitness for the purpose here used can be judged from the following experiment: Pure distilled water was boiled and while still warm crystallized iodide and iodate were added and dissolved. After 15 minutes in bright diffuse daylight a tinge of color due to free iodine had developed, but so slight as to be beyond titrimetric measurement with ordinary concentrations. After 30 minutes, the color still being very pale, solution of soluble starch was added. It was then found that one drop of a thiosulfate solution of approximately 0.07 *N* was in excess of the amount needed to discharge the blue color. The mixture stood, still colorless, for seven hours from the first mixture of the salts.

TABLE I.—STANDARDIZATION OF THIOSULFATE BY IODATE.

No.	Na ₂ S ₂ O ₃ . Cc.	Conc. acetic. Cc.	KI. Grams.	Vol. Cc.
1.....	20.90	{ 10	2.8	60
2.....	20.92		2.8	63
3.....	20.93		2.8	63
4.....	20.87		2.8	60
5.....	20.93		2.8	60
6.....	20.92		2.8	61
7.....	20.92	{ 5	2.8	63
8.....	20.89		2.8	63
9.....	20.88	{ 3	2.8	63
10.....	20.93		2.8	63
Conc. H ₂ SO ₄ .				
11.....	21.04	{ 1	2.8	65
12.....	21.00		2.8	65
13.....	21.00	1	2.8	65
14.....	21.04	{ 2	2.8	61
15.....	21.04		2.8	61
16.....	21.05		2.8	61
17.....	21.05		2.8	61
Conc. acetic.				
18.....	20.90	10	5.5	60
19.....	20.92			

A large stock solution of thiosulfate, approximately 0.2 *N*, had been prepared about one week when the following standardizations were made: Calibrated burets were used, deliveries being made according to the time and manner specified by the German Imperial Commission.¹ All solutions, however, were used at the same room temperature which introduces no error into the comparative values on the iodometric and

¹ Schloesser, W., "Beiträge zur Prüfung maasanalytischen Messgeräte." *Z. anal. Chem.*, 46, 392-414 (1907) and references. Also various reports of the German Imperial Commission in *Z. angew. Chem.*, 1893, p. 557; 1897, p. 643; 1904, p. 1746. Also Schloesser, *ibid.*, 1903, p. 953ff.

the copper standards. The potassium iodate was dried in an oven, cooled in a desiccator and a weight of 14.8302 g. was dissolved to a volume of two liters. This standard solution had therefore a value of 0.20786 N. From this solution, in a buret, 20 cc. volumes were delivered into 200 cc. Erlenmeyer flasks. Distilled water 20 cc., concentrated acetic acid 10 cc., and then crystallized potassium iodide about 2.8 g. were added in the order named. The free iodine was titrated with the thiosulfate, using soluble starch indicator at the end. Experiments with sulfuric acid were also made on the same plan as with acetic. The results are tabulated in Table I.

The accuracy and consistency of the data obtained with acetic acid are highly satisfactory. Since the normality of the potassium iodate

solution was 0.20786 that of the thiosulfate $= \frac{20.00}{20.91} \times 0.20786 =$

0.19880 N. Since a normal solution of copper is equivalent to 63.57 grams per liter, the value of the thiosulfate solution in terms of copper,

calculated according to the theory of normalities $= \frac{20.00}{20.91} \times 0.20786 \times$

63.57 = 12.633 grams of Cu per liter, *i. e.*, the standard value of the thiosulfate is 12.633 mg. of copper per cubic centimeter. This value is attended by a very small limit of error, as shown by the deviations from the mean and is at least 0.6% less than the lowest values calculated from the copper standardizations given below.

With reference to the conditions of this standardization it should be noted that these were the same for all the titrations except the acidity. Acetic acid permits of a wide range in the amount of acid present without variation in the results. Sulfuric acid causes the liberation of more iodine as the concentration of acid increases. Since its concentration markedly influences the results it is evidently not as well adapted to this purpose as acetic. Furthermore, the titration results with acetic acid are lower and consequently it gives a higher normality than would sulfuric acid. If the values with the latter acid were adopted the copper value of the thiosulfate as determined by iodine (from iodate) would differ still more than has been above stated from the copper value as determined by means of copper.

(4) *The Influence of the Concentration of Acids and of Salts on the Results of the Iodide Method.*—Before making direct experiments on the standardization of thiosulfate by copper, the results of the following experiments will be given which show the influence, not simply of acid but of an excess of acid adjusted to the conditions if correct results are to be obtained by the iodide method. This influence is especially evident in solutions which contain a quantity of ionizing salts and particularly in the neutralized alkaline tartrate solutions or filtrates occurring

in sugar analysis. This is especially the place where the iodide method should serve on account of its possibilities of accuracy and rapidity. Moreover, since Gooch and Heath¹ set a maximum limit of about 0.3 g. of copper for a titration under the conditions which they investigated it was important to determine whether the method could be extended with accuracy to the larger amounts which occur in some methods of sugar analysis.

In a method of sugar analysis here tested, a published report of which will shortly follow, the total volume for reduction was always 60 cc. This consisted of 20 cc. of Allihn's alkaline tartrate solution + 20 cc. of Fehling's copper sulfate solution + 20 cc. either of water as in a blank determination or of an aqueous sugar solution. After reduction with sugar (under conditions subsequently to be described) the mixture, while still quite hot, is filtered free from cuprous oxide through a suitable filter. After washing, the filtrate (alkaline copper solution) has a volume of 70–75 cc.

The question of how to acidify this solution properly for the iodide method was approached through the following preliminary tests on the degree of acidity. To 20 cc. of the alkaline tartrate solution were added 40 cc. of water and some phenolphthalein. Concentrated sulfuric acid was added by drops from a graduated pipet. With 2.65 cc. of acid the solution became acid to phenolphthalein, but was neutral to litmus. With 2.75 cc. distinct acidity to litmus occurred. In another test with methyl orange, acidity occurred with 3.35 cc. These data indicate, of course, the conversion of alkali to acid salt shown by phenolphthalein and litmus with 2.75 cc. of acid and to neutral salt shown by methyl orange with 3.35 cc. of acid. They afford an excellent basis for testing the influence of acids and salts upon the results of copper measurement by the iodide method, since they exhibit gradual variations of both constituents. The 70–75 cc. of alkaline tartrate and copper above described were now treated in separate samples with 2.7, 3.0, 3.4, 4.0, and 5.0 cc. of concentrated sulfuric acid. With the temperature of these liquids at approximately 20°, 10 cc. of a saturated solution of potassium iodide were added and then they were titrated with the same stock of sodium thiosulfate. With 2.7 cc. of acid the evolution of iodine was imperfect and the mixture became of a dirty green color. The end-point was so slow and uncertain as to be practically useless for accuracy. Both with 2.7 cc. and with 3.0 cc. of acid the annoying phenomenon of false end-points occurred frequently before the final and slowly obtained end-point was reached. Evidently simple acidity to litmus is not sufficient for accuracy when a quantity of salts is present. It may be noted in passing that with less than 2.45 cc. of acid there was a considerable

¹ *Loc. cit.*, p. 74.

precipitation of salts upon cooling, which ceased to occur with 4.0 and 5.0 cc. of acid. With additions of 3.45 cc. or more of acid the evolution of iodine was always good and the end-point very sharp, as the close agreement of duplicates in the following table shows:

TABLE II.—INFLUENCE OF ACID ON THE RESULTS BY THE IODIDE METHOD IN THE PRESENCE OF MUCH TARTRATE AND SULFATE.

Conc. H ₂ SO ₄ . Cc.	Acid/Vol.	Na ₂ S ₂ O ₃ . Cc.	Conc. H ₂ SO ₄ . Cc.	Acid/Vol.	Na ₂ S ₂ O ₃ . Cc.
3.....	1/40	27.60	4.....	1/30	27.85
3.....	1/40	27.41	4.....	1/30	27.85
3.....	1/40	27.34	4.....	1/30	27.84
3.....	1/40	27.35			—
	Average,	27.40		Average,	27.85
3.45.....	1/29	27.87	5.....	1/24	27.92
3.45.....	1/29	27.82	5.....	1/24	27.94
3.45.....	1/29	27.73	5.....	1/24	27.92
3.45.....	1/29	27.69			—
	Average,	27.78		Average,	27.93

It is highly important that the reagents be mixed in the order above mentioned, especially that the concentrated acid be not added until the dilution with the amount of water to be used has been made. Salts are thus held in solution which would otherwise precipitate, thus causing different or irregular titration values dependent on salt concentration, as shown in Table III. The results will also be different if the potassium iodide be first added to the alkaline liquid and the acid subsequently, even though the acid is previously diluted. It should also be noted that such conditions are sought as will bring the reaction to a close quickly, so that titration may follow at once after the addition of potassium iodide and thorough mixing.

In the experiments recorded in the following table the volume at the end of titration was always approximately 120 cc. and 10 cc. of saturated solution of pure potassium iodide were uniformly used. Each titration also was made on two deliveries of the electrolytically standardized solution of copper sulfate taken by means of two deliveries of the automatic pipet.

The data above tabulated show clearly that the values obtained by the iodide method are easily influenced by the amount of acidity or of a salt in which the evolution of iodine occurs. The potassium iodide here used was the same as that which was tested as described on p. 437. If a way cannot be found of using the iodide method satisfactorily with this high grade of reagents then the method must be pronounced impracticable where accuracy is required. However, impurity of reagents would

scarcely account for the gradation of results shown by the table. There is a discrepancy of 4 parts in 279, or about 1.4% between the highest and lowest values. Even if we start from the methyl orange neutral point at about 3.35 cc. of acid there is an increase in the evolution of iodine with increasing acidity. Now by electrolytic determination each of the analyses of this table represents two deliveries of 176.9 milligrams of copper = 353.8 milligrams of copper. The question arises, which of these averages, if any, correctly represents the copper, or *vice versa*, if the thiosulfate were to be standardized for the measurement of copper, which of these averages should be used as a divisor for the 353.8 milligrams of copper. Evidently there is need of a criterion by which to judge not only of the accuracy of the standardization in the iodide method but also of the accuracy of its indications in those numerous cases where varying acidity and salt content occur.

In order to test further the influence of salts a series of experiments was made in which slightly more of a given salt than would dissolve was added to each titration liquid after acidification. The only exception is ammonium nitrate, of which 4 grams were used in a final volume of 120 cc. Potassium iodide was then added (temperature about 20°) and titration followed. These were estimations of pure solutions of copper without the presence of the alkali or the tartrate of the preceding series. The acidities were such as succeeding data discussed on pp. 442ff. will show to be capable of giving correct results on pure solutions of copper when these salts are absent. Two deliveries of copper sulfate from the automatic pipet = $2 \times 176.9 = 353.8$ mg. of copper were used in each titration. The ratio of added acid to final volume Acid/Vol. is calculated uniformly on an approximate volume of 120 cc.

The table includes, among others, those salts which different authors have either added to the titration liquids for the iodide method in their special procedures or which have been formed in the processes used. In pure solutions as a control test these salts did not act upon potassium iodide.

The above data show that even when the amount of acid and all other conditions except salt content are kept constant the results of the iodide method are affected by the presence of salts. In those cases where sodium acetate without added acid was used the development of iodine was so imperfect as to affect the certainty of the end-point, which resulted in the poor agreement of the duplicates. By comparison with the first four titrations where results are given with neutral reaction and with acetic acid, but without addition of salts, it is seen to what extent the titrations in the presence of these salts varied from this standard.

All the preceding data lead to the conclusion that the condition of acidity or of salt content, as well as both combined, as in the copper

liquids of sugar analyses, and in other practical cases, may affect the accuracy of the results of the iodide method.

TABLE III.—INFLUENCE OF SALTS AND ACID ON THE RESULTS BY THE IODIDE METHOD.

Salt added.	Acid added.	Acid/Vol.	Na ₂ S ₂ O ₃ . Cc.	Vol. Cc.
None	Neutral	0/120	27.86	117
"	"	0/120	27.84	119
"	20 cc. conc. acetic	1/6	27.86	120
"	20 cc. "	1/6	27.85	118
Na ₂ (C ₂ H ₃ O ₂)	None	0/120	27.88	125
"	"	0/120	27.67	123
"	20 cc. conc. acetic	1/6	27.96	124
"	20 cc. "	1/6	27.95	124
"	2 cc. conc. H ₂ SO ₄	1/60	27.94	126
"	2 cc. "	1/60	27.95	126
NH ₄ (C ₂ H ₃ O ₂)	20 cc. conc. acetic	1/6	27.87	120
"	20 cc. "	1/6	27.99	123
"	20 cc. "	1/6	27.97	100
Zn(C ₂ H ₃ O ₂) ₂	None	0/120	26.68	118
"	"	0/120	26.51	119
"	20 cc. conc. acetic	1/6	27.97	118
"	20 cc. "	1/6	27.98	119
"	2 cc. conc. H ₂ SO ₄	1/60	27.98	123
"	2 cc. "	1/60	27.94	122
Na ₂ SO ₄	20 cc. conc. acetic	1/6	27.55	120
"	20 cc. "	1/6	27.59	120
K ₂ SO ₄	2 cc. conc. H ₂ SO ₄	1/60	27.91	120
"	2 cc. "	1/60	27.98	120
NH ₄ NO ₃	20 cc. "	1/6	27.78	118
"	20 cc. "	1/6	27.74	118
KCl	2 cc. conc. H ₂ SO ₄	1/60	28.11	120
Pure sucrose	20 cc. conc. acetic	1/6	27.86	120
"	20 cc. "	1/6	27.83	120
"	20 cc. "	1/6	27.85	120

(5) *The Standardization of Thiosulfate by Copper and the Influence of Varying Concentrations and Volumes.*—The next series of experiments was made for the purpose of standardizing the same thiosulfate solution heretofore used by means of electrolytically standardized copper solutions. Excess of salts other than reagents is excluded, but varying conditions of acidity were tested. The results of this series, together with those which precede, were expected to provide the basis for the selection of standard conditions for accuracy.

The following results show the disturbing effect of varying acidity even when the titration liquids are free from excess of salts. As in preceding experiments, they uniformly show an increasing development of iodine with increasing acidity. If, again, the results under conditions of neutrality be made the basis of comparison it appears that a small concentration of sulfuric acid does not cause variation from this basal value.

TABLE IV.—STANDARDIZATION OF THIOSULFATE BY COPPER.

Acid added.	Acid/Vol.	CuSO ₄ . Del.	Na ₂ S ₂ O ₃ . Cc.	Aver. Na ₂ S ₂ O ₃ . Cc.	Sat. KI. Cc.	Vol. Cc.
Neutral.....	0/120	2	28.82	27.83	{ 10	120
Neutral.....	0/120	2	27.85		{ 10	120
10 cc. acetic	1/6	1	13.90	13.92 (27.84)	{ 5	60
10 cc. acetic	1/6	1	13.93		{ 5	60
20 cc. acetic	1/6	2	27.83	27.85	{	120
20 cc. acetic	1/6	2	27.86		{	120
2 cc. H ₂ SO ₄	1/60	2	27.85	27.83	{ 10	120
2 cc. acetic	1/60	2	27.82		{ 10	120
2 cc. H ₂ SO ₄	1/30	1	13.95	13.94 (27.88)	{ 5	60
2 cc. H ₂ SO ₄	1/30	1	13.93		{ 5	60
2 cc. H ₂ SO ₄	1/30	1	13.94	13.95 (27.90)	{ 5	60
2 cc. H ₂ SO ₄	1/30	1	13.95		{ 5	60
5 cc. H ₂ SO ₄	1/24	2	27.89	27.88	{ 10	120
5 cc. H ₂ SO ₄	1/24	2	27.87		{ 10	120
6 cc. H ₂ SO ₄	1/25	2	27.85	27.85	10	150
10 cc. H ₂ SO ₄	1/15	2	27.89	27.89	10	150

TABLE V.—STANDARDIZATION OF THIOSULFATE BY COPPER.

Acid added.	Acid/Vol.	CuSO ₄ . Del.	Na ₂ S ₂ O ₃ . Cc.	Aver. Na ₂ S ₂ O ₃ . Cc.	Sat. KI. Cc.	Vol. Cc.
Neutral.....	0/120	2	27.84	27.85	{ 10	120
Neutral.....	0/120	2	27.85		{ 10	120
2 cc. H ₂ SO ₄	1/60	2	27.81	27.83	{ 10	120
2 cc. H ₂ SO ₄	1/60	2	27.85		{ 10	120
2 cc. H ₂ SO ₄	1/70	2	27.79	27.80	{ 10	140
2 cc. H ₂ SO ₄	1/60	2	27.80		{ 10	120
2 cc. H ₂ SO ₄	1/30	1	13.95	13.94 (27.88)	{ 5	60
2 cc. H ₂ SO ₄	1/30	1	13.93		{ 5	60
5 cc. H ₂ SO ₄	1/28	2	27.89	27.91	{ 10	140
5 cc. H ₂ SO ₄	1/28	2	27.92		{ 10	140
5 cc. H ₂ SO ₄	1/24	2	27.86	27.87	{ 10	120
5 cc. H ₂ SO ₄	1/24	2	27.88		{ 10	120
5 cc. H ₂ SO ₄	1/12	1	14.00	14.01 (28.02)	{ 5	60
5 cc. H ₂ SO ₄	1/12	1	14.02		{ 5	60

This concentration seems to be in the vicinity of 1/60 of the total volume at the end of titration. As before, a high concentration of acetic acid, *e. g.*, 1/6 of the final volume, does not affect the values obtained. These results, pertaining to small concentrations of sulfuric acid and large concentrations of acetic acid, agree with the findings of Gooch and Heath.¹ These authors set a maximum limit of 2 cc. of concentrated acid in 50 cc. of liquid, *i. e.*, a proportion of 1/25. Bray and MacKay² considered the proportions used by Gooch and Heath too large, as they found the development

¹ *Loc. cit.*, p. 71.

² *Ibid.*, p. 1199.

of iodine under the influence of the reagents above to be large enough to be easily measurable. Bray and MacKay¹ also found that acetic acid had practically no influence on the results compared with mineral acids. The method pursued in obtaining the above tabular values, *viz.*, that of performing titrations with varying amounts of acid, show the influence of the acid under exactly the conditions of analysis. These data show that the maximum proportion of 1/25 set by Gooch and Heath is distinctly too large, and these authors state as follows (p. 74) with reference to acid: "We find no ground for the inference of Moser² that the presence of acid, best sulfuric acid, is necessary to the attainment of good results at all volumes excepting the most concentrated; and there appears to be no reason why the addition of small amounts of acid should increase the amount of iodine liberated, if the potassium iodide is free from iodate or other oxidizer. We are wholly unable to offer any explanation for Moser's extraordinary observation, quite contrary to our own, that variation in the amounts of $\frac{10N}{1} \text{H}_2\text{SO}_4$, from 1^{cm}³ to 100^{cm}³ (0.49 gram to 49 gram) for 50^{cm}³ of a solution of copper sulfate, is practically without effect in the treatment by potassium iodide."

All these accounts taken together indicate that possibly no acid is necessary, *i. e.*, that a neutral reaction is always adequate for the iodide reaction, and that in any case a low concentration of mineral acid is permissible. But since the tabular results here presented show the variety of values that may be obtained, there is wanting a delimitation of conditions that would result in invariable accuracy. In order to obtain a basis for the correct standardization of these conditions it is here proposed that the results obtained with neutral solutions and with moderate proportions of acetic acid (*e. g.*, 1 volume in 6) and in the practical absence of salts be regarded as the correct standard. These two conditions have been found in agreement by other experimenters. In the above tables they have the following values, for neutral titration liquids: 27.86, 27.84, 27.84, 27.85, 27.82, 27.85 = average of 27.84 cc. with an average deviation from the mean of 0.01 cc. For acetic acid titrations with a proportion of 1 to 6: 27.86, 27.85, 27.80, 27.86, 27.83, 27.86 = average of 27.84 cc. with an average deviation from the mean of 0.02 cc. Under these standard conditions then 27.84 cc. of thiosulfate = $2 \times 176.9 = 353.8$ mg. of copper. Therefore the thiosulfate has a value of 12.708 mg. of copper per cc. The value 12.708 is to be compared with 12.633 by iodine (from iodate) found on p. 438. This is a discrepancy of 75 parts in 1270 = 0.6%. The results with sulfuric acid in the concentration of 1 to 60 and in the practical absence of salts may now be examined and

¹ *Loc. cit.*, p. 1199.

² *Z. anal. Chem.*, 43, 597 (1904).

they have the following values: 27.85, 27.82, 27.81, 27.85, 27.79, 27.80 = average of 27.82 cc. with an average deviation from the mean of 0.02 cc. This agrees well with the results under the above standard conditions with neutrality or with acetic acid. All the other values with sulfuric acid would give different results. If now the results with sulfuric acid in the absence of tartrate and sulfate be examined, it is found that when 4 cc. of sulfuric acid were used the result, 27.85 cc., was the same as under the standard neutral or acetic acid conditions. Hence with this amount of acid the alkaline tartrate solution of copper can be correctly estimated by the iodide method, so that the results essentially agree with those of electrolysis. All the other concentrations of sulfuric acid that were tried would result in erroneous values.

The principle here involved is that the copper measurements by the thiosulfate must give the same values in the presence of salts and acids as in their absence and that these results must in all cases be the same as those of electrolysis. Where the salt mixture can be obtained separate from the copper to be estimated as with the alkaline tartrate solutions of sugar analysis, this end is easily reached by standardizing the thiosulfate with and without the salt or acid to be tested. The amount of acid is adjusted to give the same result as the control standardization. When the amount of acid and salt, even though mixed and unknown, are constant for routine analyses, electrolytic controls once made suffice to show the measuring power of the thiosulfate in comparison with the standard conditions with neutrality or with acetic acid.

When the conditions presented are those of unknown and miscellaneous samples, accuracy can still be attained by a method of quantitative compensation described on p. 448.

Finally, with reference to the discrepancy between the standard values by iodine (from iodate) and by copper the following considerations should be made. If the standardizations were made under the use of mineral acids the development of iodine would be greater in both cases, as shown by all the tables, and consequently the standard values of both in terms of copper would be correspondingly depressed but their relation would not be materially altered. The discrepancy then is due in the first instance to the development of too little iodine by the copper method, thus giving a comparatively high result for the value of the thiosulfate. Bray and MacKay¹ have suggested as the cause of this difference, the absorption of iodine by the cuprous iodide precipitate, thus withdrawing it from the action of thiosulfate. Some of the experiments tabulated below show the result when the amount of potassium iodide is sufficient to dissolve all the precipitated cuprous iodide, thus removing the possibility of absorption.

¹ *Loc. cit.*, p. 1199.

TABLE VI.—INFLUENCE OF THE CONCENTRATION OF COPPER ON THE RESULTS OF THE IODIDE METHOD.

No.	CuSO ₄ .	Cu. Mg.	Na ₂ S ₂ O ₂ . Cc.	Aver. Na ₂ S ₂ O ₂ . Cc.	Vol. Cc.	Sat. KI. Cc.	Conc. acetic acid. Cc.	Calc. Na ₂ S ₂ O ₂ . Cc.	Diff. Cc.
1	2 Del.	353.8	28.85	27.86	120	10.0	20	(27.86)
2	2 Del.		27.86						
3	2 Del.	353.8	27.85						
4	2 Del.		27.84	27.85	120	10.0	20	(27.85)
5	2 Del.		27.85						
6	40/100 of 4 Del. ...	283.0	22.28						
7	40/100 of 4 Del. ...	283.0	22.29	22.29	120	10.0	20	22.29	0
8	30/100 of 4 Del. ...	212.8	16.73						
9	30/100 of 4 Del. ...	212.8	16.72						
10	20/100 of 4 Del. ...	141.5	11.15	11.16	120	10.0	20	11.14	+0.02
11	20/100 of 4 Del. ...	141.5	11.16						
12	10/100 of 4 Del. ...	70.8	5.60						
13	10/100 of 4 Del. ...	70.8	5.59	5.60	121	10.0	20	5.57	+0.03
14	10/100 of 4 Del. ...	70.8	5.60						
15	12/100 of 4 Del. ...	84.9	6.74						
16	12/100 of 4 Del. ...	84.9	6.70	6.71	118	10.0	20	6.68	+0.03
17	12/100 of 4 Del. ...	84.9	6.68						
18	10/100 of 4 Del. ...	70.8	5.56						
19	10/100 of 4 Del. ...	70.8	5.58	5.57	{ 118 } { 116 }	10.0	20	5.57	0
20	10/100 of 4 Del. ...	70.8	5.60						
21	10/100 of 4 Del. ...	70.8	5.59						
22	10/100 of 4 Del. ...	70.8	5.58	5.57	25	5.0	4	5.57	+0.03
23	10/100 of 4 Del. ...	70.8	5.55						
24	8/100 of 4 Del. ...	56.6	4.43						
25	8/100 of 4 Del. ...	56.6	4.45	4.44	119	10.0	20	4.46	—0.02
26	8/100 of 4 Del. ...	56.6	4.46						
27	8/100 of 4 Del. ...	56.6	4.44						
28	6/100 of 4 Del. ...	42.5	3.36	3.36	124	20.0	20	3.34	+0.02
29	6/100 of 4 Del. ...	42.5	3.35						
30	5/100 of 4 Del. ...	35.4	2.76						
31	5/100 of 4 Del. ...	35.4	2.80	3.78	{ 116 } { 118 } { 118 }	10.0	20	2.79	—0.01
32	5/100 of 4 Del. ...	35.4	2.79						
33	5/100 of 4 Del. ...	35.4	2.78						
34	5/100 of 4 Del. ...	35.4	2.79	2.79	117	10.0	20	2.79	0
35	4/100 of 4 Del. ...	28.3	2.28						
36	4/100 of 4 Del. ...	28.3	2.24						
37	4/100 of 4 Del. ...	28.3	2.24	2.25	117	10.0	20	2.23	+0.02
38	4/100 of 4 Del. ...	28.3	2.24						

Here also are tabulated the results of experiments so planned as to show to what extent the evolution of iodine in the iodide method is affected by the relative concentrations of copper or by the relative volumes in which the reaction occurs. In most of the experiments four deliveries

of the standardized pure copper sulfate (176.9 mg. Cu each) were run into a 100 cc. volumetric flask and made to the mark with distilled water. This solution was then placed in a buret from which the proportions shown by column 2 were taken. Each portion was then estimated by the iodide method as indicated by the table.

The basis of comparison for all the above results is the largest titration of copper made under constant conditions on the constant volume of approximately 120 cc. This amount is 27.86 cc. and has been verified by other titrations. The calculated titrations of column 9 were obtained on the supposition that aliquot volumes would give strictly proportional titrations. The differences of column 10 show the variation of the experimentally found values of column 5 from those calculated in column 9. The results clearly show that such proportionality does exist and that the results obtained by the iodide method under controlled condition of reagents are strictly comparable for large and small amounts of copper.

The concentration of copper expressed as $\frac{\text{Cu. mg.}}{\text{Vol. cc.}}$ for the determinations

in 120 cc. vary from $\frac{354}{120}$ to $\frac{28}{120}$, i. e., from 2.95 to 0.23. The limits of error, especially with the smaller amounts of copper, are surprisingly small when the unfavorable conditions of large volume and concentrated thiosulfate solution compared to the small amount of copper to be estimated are considered. For other reasons small amounts of copper should, of course, be measured with dilute thiosulfate in a small volume. The severest test for the present proposition was to maintain the same large volume and comparatively concentrated thiosulfate for widely varying amounts of copper.

The results above tabulated also permit the following observations on absorption of iodine by cuprous iodide. In experiments Nos. 1-25 the concentration of potassium iodide, as shown by the table, was not sufficient to hold all of the cuprous iodide in solution. In experiments 26-38 complete solution occurred. Although the amounts of copper here determined were small and the conditions unfavorable, as above described, the results found and calculated agree very closely. However, the basis of calculation was the value 27.85 cc. obtained with the large amount of copper of 353.8 milligrams where solid cuprous iodide occurred in abundance and could have permitted absorption of iodine. The exact proportionality of the results show that such absorption did not occur in any of these determinations, even when abundance of solid cuprous iodide was present. Hence this possible source of error does not exist in the method as here followed and the factor of absorption does not explain the discrepancy between the iodine and the copper standardiza-

tions of thiosulfate. The possibility that cuprous iodide may absorb some iodine under certain conditions is, of course, not denied.

(6) *General Conclusions on the Iodide Method.*—A salient characteristic of the iodide method from the standpoint of accurate, electrolytically controlled copper measurement is its sensitiveness to change of conditions. This fact finds its explanation in the dependence of the method upon a sensitive equilibrium reaction. The ready variability of values by the iodide method according to concentration of acid and of salts, and according to the selection of the standard values of the thiosulfate, etc., renders it difficult to guarantee its accuracy without full knowledge of the special conditions involved in each analysis. This latter necessity ranks the iodide method below the electrolytic method in general applicability, when a high degree of accuracy is required.

Very accurate measurements of copper can be made by the iodide method with the procedure previously described and under the following provisions: (1) The conditions of the analyses to be made can frequently be so adjusted that the same values for thiosulfate hold as for the special conditions of the original standardization of the thiosulfate. The copper of the alkaline tartrate solutions from sugar analyses can thus be accurately determined by adjusting once for all the degree of acidity. (2) The thiosulfate is empirically standardized for the special conditions of a series of analyses by the electrolysis of a sample of the frequently recurring routine solutions which present a repetition of the same conditions. (3) The influence of varying conditions which may not be in harmony with those of the original standardization of the thiosulfate can be tested and quantitatively compensated by the following method: The maximum amount of the unknown copper solution is first titrated and secondly, to half of this amount is added an equal and exactly known amount of pure standard solution of copper and another titration is then made with the same final volume and reagents. The divergence from the first titration and its sign are then noted and twice this amount is applied as a correction to the first value. The corrected thiosulfate value thus found may now with accuracy be multiplied by the standard value of the thiosulfate obtained under standard conditions. When the amount of copper is small a smaller volume, *e. g.*, 50 cc. and a more dilute thiosulfate, *e. g.*, of a value of about 3 mg. of copper per cubic centimeter, provides corresponding conditions for the above procedure.

The iodide method can be made to give exceedingly accurate results, comparable within limits of error, with those of electrolysis. It requires, however, rigid control of pure copper or by electrolysis, which control must be extended to the detailed conditions of its application in order to obtain results concordant with the theory.

6. Summary of the Conditions of the Iodide Method for the Greatest Accuracy and Sensitivity Especially in the Analysis of Alkaline Tartrate Solutions.

(1) *Introduction*.—A highly valuable experimental study of the conditions for the iodide method was made by Gooch and Heath¹ where also the principal developments of the preceding literature are taken into consideration. The earlier paper of Moser² is also a valuable contribution on the iodide method. From these accounts, as well as from the results of numerous copper determinations made by myself, the desirable conditions for the iodide method may be summarized as follows:

(2) *The Concentration of Potassium Iodide*.—The concentration of the potassium iodide should be high in comparison to the equivalent (see equation) of copper present, regardless of whether the absolute amount of copper be small or large. The reaction between copper sulfate and potassium iodide does not run to completeness unless there is present a considerable excess of the iodide. The most important point is that the concentration of iodide be high in relation to the final volume at the end of titration and not simply with reference to the absolute amount of copper present. This is a condition of great importance, which was well developed by Gooch and Heath.³

I use a solution of potassium iodide which is in saturated condition when the solution has reached room temperature. It has been found that when this solution is kept in the dark instead of on the laboratory table, and when stoppered, it liberates iodine much less rapidly. Free iodine should be removed with dilute thiosulfate solution. Ten cubic centimeters of such a saturated solution weighed 17.120 g. and after evaporation to dryness left a residue of 10.840 g. Hence 1 cc. represents about 1.1 g. of the iodide. Since comparatively large quantities must be used, the titrated liquids, if numerous determinations are made, should be saved for the recovery of iodine as described below.⁴ In this

¹ *Am. J. Sci.*, 24, 65–74 (1907).

² *Z. anal. Chem.*, 43, 597–608 (1904).

³ *Loc. cit.*

⁴ The following method for the recovery or rough evaluation of waste titration liquids containing iodine was found efficient and convenient. The titrated liquids including the cuprous iodide are distilled from a tubulated retort carrying a safety tube. The open end of the retort is immersed in cold water. Upon boiling the liquid with manganese dioxide and sulfuric acid, free iodine passes over and is collected in the water, some also adhering to the neck of the retort. The whole distillate is filtered through glass wool and the iodine is dried on a porous plate. The iodine may be converted to hydriodic acid by the method of Winkler, as follows: It is dissolved in a quantity of carbon tetrachloride which is covered with a layer of water. Hydrogen sulfide is passed and as the iodine is removed by the accumulation of hydriodic acid in the watery layer, more iodine is added to the tetrachloride. The action is slow at first, but the process works very satisfactorily. When the quantity of these waste titration liquids is large it may be advisable to sell the evaluated material.

work approximately 120 cc. at the end of titration was the most frequently used volume, and for this 6–10 cc. of the iodide solution were taken. For titrations in a volume of 60 cc. or less, 5 cc. of iodide solution were generally used. Beyond a certain limit included within the above amounts, an increase in potassium iodide no longer affects the results, but a very great excess should be avoided as liable to produce the same effect as high salt concentration (see Table III, p. 442). Occasionally when the amount of copper was small the resulting cuprous iodide was completely dissolved by the iodide, but this does not vitiate the results.

These titrations were made with an approximately uniform volume of 120 cc. at the end of titration and with 5 cc. of concentrated sulfuric acid. They were all made on the same amount of copper sulfate solution, *viz.*, one delivery of the automatic pipet:

TABLE VII.—INFLUENCE OF THE CONCENTRATION OF POTASSIUM IODIDE ON THE RESULTS OF THE IODIDE METHOD.

Sat. KI. Cc.	KI/Vol.	Na ₂ S ₂ O ₃ titrat. Cc.	Sat. KI. Cc.	KI/Vol.	Na ₂ S ₂ O ₃ titrat. Cc.
6	1/20	13.98	2	1/60	13.94
5	1/24	13.98	1	1/120	13.91
3	1/40	13.94	0.5	1/240	9.66
			4	1/30	13.97

(3) *The Degree of Acidity.*—A second desirable condition is the presence of a limited but indefinit concentration of hydrogen ion. Nitric or even hydrochloric acid¹ is undesirable for this purpose. When no considerable amount of electrolytes is present, acetic acid within a wide range of concentration may be used, or sulfuric acid in relatively small amount. Sulfuric and not acetic acid should be used for acidifying the alkaline reduction mixtures occurring in sugar analyses. These also contain a considerable concentration of Rochelle salt which, together with the salt formed by acidification, tend to depress the ionization of the excess of acid. With acetic acid this depression, especially when the volume is small, is so great that the liberation of iodine is not free and rapid. Under these circumstances a premature end-point may occur with the thiosulfate, more iodine being liberated soon after the apparent end-point, or the whole reaction and titration may proceed so slowly as to be uncertain. Sulfuric acid should be used in small but sufficient excess to give a prompt and complete evolution of iodine. The result is due to its greater ionization than that of acetic acid.

In any case prompt evolution of iodine, a yellow to brown, not a greenish color of the reaction mixture, and a rapidly attained end-point with thiosulfate are evidences of sufficient excess of acid. Too great an ex-

¹ See Moser, *Loc. cit.*, p. 600.

cess of acid would, as Gooch and Heath¹ and Bray and MacKay² observed, liberate iodine from potassium iodide in the presence of air. Possibly this source of error always occurs in the iodide method, but its amount should be negligibly small during the time consumed in a titration. That iodine develops in a longer period of time and redevelops after the titrations are finished has but little practical significance.

(4) *The Loss of Iodine by Volatilization.*—Another condition for the accuracy of any iodine titrations is that they be performed in narrow-necked Erlenmeyer flasks of the smallest convenient volume, *e. g.*, of 100 to 300 cc. and, it need scarcely be added, the temperature should not exceed that of the room. It was not found necessary to stopper the vessels used under these conditions, especially when the liberation and the titration of the iodine altogether occupied only a few minutes.

(5) *The Volume of the Titration Mixture.*—The practical question arises as to what is the most favorable concentration of sodium thiosulfate with which to titrate the liberated iodine under any conditions of dilution. The answer depends primarily upon the volume of liquid in which *at the end of the titration* one drop of thiosulfate of any proposed concentration will still produce a definitely perceptible change of color called the end-point of the titration. Thus the conditions for the greatest accuracy are summarized as follows: The largest amount of substance (copper) to be estimated, contained in the smallest volume, should be titrated with the most dilute thiosulfate that gives a good end-point. When any one of these three conditions is determined, the other two can be adjusted for the maximum accuracy which the determined condition permits.

One of the most frequent and least perceived of the errors made by the iodide method is the failure to use sufficient potassium iodide and acid when volumes above 100 cc. are obtained at the end of titration. Only by observing this condition can comparable results be obtained for the same amount of copper in large and in small volumes.

(6) *The Starch-iodine End-point in the Presence of Suspended Cuprous Iodide.*—A comparison of the relative usefulness of various concentrations of thiosulfate involves a consideration of the nature of the end-point in the iodide method. The presence of a greater or less quantity of the precipitated slightly yellowish white cuprous iodide considerably modifies this end-point from that of a simple iodine titration where the final change from blue to colorless is very easily determined. In the presence of cuprous iodide and starch the mixture, shortly before the end of the titration, assumes a chocolate-brown color, which changes to a light cream-white as the last necessary drop of thiosulfate is added. The end-

¹ *Loc. cit.*, pp. 70–71.

² *Ibid.*, p. 1199.

point *has already occurred* when another drop of thiosulfate does not diminish the prevalent very light shade of the mixture. The recognition of the end-point must be learned by some practice. It can be satisfactorily obtained in good diffuse daylight, as well as by artificial light, by working over a white surface. It is by no means uncertain or indefinite, as the very close agreement of repeated titrations by several observers shows. Bray and MacKay¹ found that the change of color of the particles of suspended precipitate was a good indication of this end-point. In these experiments the phenomenon of colored particles was not observed when fresh soluble starch was used, but only with an indicator of common boiled starch (used only for trial) and of older solutions of soluble starch. The "spot test," contrary to the opinion of Moser,¹ seems to be the best of all direct indications of the end-point. So long as a drop of thiosulfate falling upon the quiet surface of the titration liquid produces a perceptible white area the end-point has not yet been reached. Practically all the titrations here reported were made with this end-point.

It is strongly urged that another buret be constantly kept at hand containing an iodine solution of practically equivalent concentration to the standard thiosulfate. This scheme is highly useful when the conditions of illumination are not favorable, or in the presence of sufficient coloring matter to disturb or when overtitration is suspected, and for the inexperienced. When the end-point is supposed to have been reached the liquid is back-titrated with the iodine to the first definitely recognizable darkening due to iodide of starch. The appearance of a color constitutes in general a better end-point for a titration than the disappearance of a color. In the former case overtitration has better defined limits. This back-titration must be done within a few minutes after the thiosulfate titration and before the liquid has stood exposed to the air long enough² to redevelop some iodine. The thiosulfate end-point is thus confirmed or corrected if necessary. For accuracy it is important to remember that all volumetric end-points are slight overtitrations and that hence the mean between the direct thiosulfate and the back-titration with iodine is more nearly correct than either alone. This error is, however, practically eliminated when, as in the residual method of sugar analysis, the quantity of reduced copper to be determined is found by taking the difference between two thiosulfate titrations, the first of which is a blank determination.

It must not be inferred from the above details and refinements that the end-point in the iodide method is not practically useful or involves any formidable difficulties.

¹ *Loc. cit.*

² See Bray and McKay, *Loc. cit.*, p. 1199.

7. Summary of Results.

(1) The different methods for the standardization of thiosulfate solutions may be classified into groups each of which gives values at variance with the others, but very constant with itself. The differences between the group values far exceed the limits of error of the individual groups. Of these groups, that which gives the same result as pure iodine must be regarded as correct for the purpose of measuring iodine *per se*. The standard value of thiosulfate determined by copper under electrolytic control is discrepant with the results of the iodine group much beyond the limits of error of either method. For accurate copper measurement by the iodide method only the empirically determined value of the thiosulfate by means of copper can be used. The copper value of the thiosulfate which can be *calculated* from the normality of the thiosulfate by iodine is therefore not applicable in the iodide method for the determination of copper.

(2) A tartrate-cyanide electrolyte for the deposition of copper has been described which permits the use of high voltage, high current density and boiling temperature compatible with a deposit of good quality. The proportion of cyanide is limited. A copper cathode may be used instead of platinum. Rapid deposition is due to the composition of the electrolyte and its continued mixture by abundant evolution of gas and from heating.

(3) A rapid method has been described for preparing solutions of copper or of its compounds for the iodide method. Solution is made in an Erlenmeyer flask by means of heat with the least necessary amount of slightly diluted nitric acid. After additions of water and powdered talcum the mixture is boiled vigorously for 5 to 10 minutes. The rapid ebullition occurring under these conditions quickly removes nitrous acid. Upon cooling and diluting, the iodide method may be applied. Sulfuric acid may be added to the nitric acid solution when a sulfate solution is desired.

(4) The accuracy of the results obtained by the iodide method is affected by (a) varying concentrations of mineral acid, (b) by the presence of salts both independently of and in conjunction with acetic or mineral acid. The results obtained in neutral and in acetic acid solutions, both of which are free from excess of salts, are concordant and thus constitute the standard of correctness. When much salt is present or when the alkaline copper solutions from sugar analyses are to be estimated, sulfuric acid rather than acetic should be used in order to obtain prompt evolution of iodine and a good end-point.

(5) It has been shown that when the conditions of the iodide method are under control: (a) the results are independent of the concentration of the copper titrated or of the volume in which the titration is made;

(b) the results on large and on small amounts of copper in the same or in different volumes are strictly comparable.

(6) It has been shown that absorption of iodine by precipitated cuprous iodide as a perceptible source of error does not occur in the iodide method as here performed. Hence this explanation of the discrepancy between the iodide and the copper standardizations of thiosulfate solutions is untenable.

(7) The ease with which the results of the iodide method are affected by a variety of conditions has been shown. Procedures have been described for testing the presence of these influences and for adjusting the conditions or quantitatively compensating them. These procedures have a general application, so that even for a high degree of accuracy the iodide method need not be limited to the special conditions of the original test analyses. The iodide method, only under control of conditions it must be emphasized, has the decided advantages of exceeding accuracy combined with rapidity.

I am under much obligation to Professor F. G. Benedict for advice and valuable criticism throughout this work. I was also ably assisted in obtaining the experimental data and in their re-examination by Mr. Richard I. Carney and Mr. Wm. F. O'Hara, of the staff of this laboratory.

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THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. III. ELECTRICAL CONDUCTANCE.

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CONTENTS.—11. Theoretical Considerations. 12. The Conductance and Viscosity Data. 13. Ionization Values at 18°. 14. Discussion of the Ionization Values at 18°. 15. Comparison of the Ionization Values at 0° and 18°. 16. Equivalent Conductance of the Separate Ions. 17. Change of the Equivalent Conductance with the Concentration.

11. Theoretical Considerations.

This article is devoted to the consideration of the electrical conductance of solutions of single salts.

The conductance of a solution may be explicitly defined in terms of the ordinary units as the number of coulombs of electricity that pass through it per second when a potential-difference of one volt exists at the electrodes. The specific conductance (L) of a solution is the conductance of one centimeter cube of it between electrodes one centimeter apart.

The conductance of aqueous solutions of salts, acids and bases (hereafter referred to by the single word "salt") seems to be almost wholly

due to the salt, since pure water is known to have only an extremely small conductance; and it is conveniently expressed in the case of solutions containing only a single salt by the concept of equivalent conductance, which is defined as follows: The equivalent conductance (Λ) of a dissolved salt is the conductance between electrodes one centimeter apart of that volume of its solution which contains one equivalent of the salt. Hence $L = C\Lambda$, where C represents the concentration of the salt in equivalents per cubic centimeter of solution.

Since, in accordance with Faraday's law and the laws of transference, flow of electricity in an electrolyte is attended by a corresponding movement of the ion-constituents, the specific conductance of a solution must be equal to the number of equivalents of the ion-constituents that pass per second through a cross section of the solution of one square centimeter area when the potential gradient is one volt per centimeter, multiplied by the charge (F coulombs) carried by one equivalent. Moreover, the number of equivalents of any ion-constituent so passing must obviously equal the product of its mobility U^1 by its concentration C (expressed in equivalents per cubic centimeter). Hence the general expression for the specific conductance of a solution containing any number of positive or negative ion-constituents A, B, \dots is

$$L = F(C_A U_A + C_B U_B + \dots)^2 \quad (23)$$

Certain factors upon which the value of the mobility U_A of any ion-constituent A must depend will now be considered. In the case in which the constituent is contained as only a single kind of ion (as would be true, for example, of either constituent of potassium sulfate, if it be assumed that the salt is dissociated only into the ions K^+ and SO_4^{--}), this value must evidently be determined: (1) by the fraction γ_A of the constituent which exists in the state of ion, and (2) by the mobility $U_{A\pm}$ of the ion itself; for it is only the free ions that actually move under the influence of the electrical potential gradient. That is,

$$U_A = \gamma_A U_{A\pm}. \quad (24)$$

For the case that there is present in the solution only a single salt which gives rise to only one positive ion B^+ and one negative ion A^- , a combination of equations (10) and (11) yields the important relation:

$$\Lambda = L/C = \gamma(U_{B+} + U_{A-})F. \quad (25)$$

In this equation C represents the concentration of the salt in equivalents per cc., Λ its equivalent conductance, and γ its ionization (that is, the fraction of it existing as free ions). This equation results from (23)

¹ The velocity under a potential-gradient of one volt per centimeter is designated the *mobility*.

² Since conductance, unlike transference, is not essentially a directive quantity, mobilities will, throughout this paper, be considered positive whether the ion moves toward the cathode or anode.

and (24), since in the special case considered $C_A = C_B = C$, and $\gamma_A = \gamma_B = \gamma$.

Equation (25) may be written in the still simpler form

$$\Lambda = \gamma(\Lambda_{B+} + \Lambda_{A-}) \quad (26)$$

by replacing FU_{B+} and FU_{A-} by the quantities Λ_{B+} and Λ_{A-} . The quantity Λ_{B+} or Λ_{A-} may be called the equivalent conductance of the ion B^+ or A^- , since it represents the conductance of that volume of the solution of any concentration which contains one equivalent weight of the (free) ion B^+ or A^- , when placed between electrodes one centimeter apart.

As the concentration of the salt approaches zero, the value of Λ is found to approach a constant maximum value Λ_0 , obviously in consequence of the facts that γ approaches unity and that Λ_{B+} and Λ_{A-} approach a constant value. Hence, for $C = 0$,

$$\Lambda_{B+} + \Lambda_{A-} = \Lambda_0. \quad (27)$$

The separate values of the mobilities or conductances of the two ions which are involved in equations (25), (26), and (27) cannot be derived from conductance values alone, since these always involve the sum of the two quantities. They can, however, be obtained by multiplying the conductance by the transference number T of the ion-constituent in question; namely:

$$\Lambda T_B = \gamma F U_{B+} = \gamma \Lambda_{B+}, \text{ and } \Lambda_0 T_B = \Lambda_{B+}. \quad (28)$$

This last equation is of much importance, as it enables values of the equivalent conductance of the separate ions to be calculated.

A consideration most important to the quantitative development of the Ionic Theory is the question of the upper limit of concentration at which equation (27) can still be regarded as substantially accurate. It is commonly assumed that it can be so regarded so long as the solution, considered as a viscous medium which offers a certain mechanical resistance to the motion of the ions through it, does not differ appreciably from pure water. And accordingly, the ionization of salts up to moderate concentrations is commonly calculated by the equation

$$\gamma = \Lambda / \Lambda_0. \quad (29)$$

This equation, unlike the preceding ones, involves a distinctly hypothetical element. While the inherent probability that this relation holds true so long as the viscosity of the solution does not differ substantially from that of pure water should not be underestimated, yet the possibility that it may become invalid at much smaller concentrations should be recognized, especially in view of possible effects caused by the electric charges on the ions, such as have been suggested by Sutherland.¹ The calculation of the ionization of salts in dilute solution from the conductance ratio Λ / Λ_0 should therefore be considered to be based upon a

¹ *Phil. Mag.*, [6], 14, 3-7 (1907).

hypothesis which has a high degree of *a priori* probability, but which must be confirmed by testing its conformity with other related phenomena. It is to be noted, moreover, that even if the ratio does not have the significance of a degree of ionization, it is a convenient empirical expression of the change of conductance with the concentration, without reference to the ionization.

Another uncertainty of a different character involved in the calculation of ionization from the conductance ratio arises from the facts that the maximum value of Λ is not fully attained even at the smallest concentrations at which accurate measurements have thus far been made, and that, therefore, Λ_0 must be obtained by extrapolation from the Λ values at higher concentrations. The best that can be done is to base this extrapolation on the assumption that the functional relation between equivalent conductance and concentration which is found empirically to hold at higher concentrations continues to hold down to zero concentration. Besides the possibility of inaccuracy in this assumption, there is the possibility of considerable error in the practical application of it to the available data, especially in the case of salts of the higher valence types where the extrapolation is a fairly long one. This practical side of the question will be discussed in a later section of this article.

At concentrations so great that the viscosity (η) of the solution differs appreciably from the viscosity (η_0) of pure water, it is to be expected, as was suggested by Arrhenius,¹ early in the history of the Ionic Theory, that the mobility and conductance of the ions will decrease, at least approximately, in the same proportion in which the viscosity increases; and therefore that the ionization is given by the following relation:

$$\gamma = \Lambda\eta/\Lambda_0\eta_0 \quad (30)$$

Although this correction for the effect of the viscosity of the solution on the mobility of the ions can not be an exact one, there is little doubt that the ratio $\Lambda\eta/\Lambda_0\eta_0$ gives a much more nearly correct measure of ionization at moderately high concentrations than does the simple conductance ratio Λ/Λ_0 .

In justification of this viscosity correction the following considerations may be presented. In the first place, the theoretical relationship of the two properties is a close one, viscosity being essentially the frictional resistance encountered by molecules of the solution in moving over one another, and ion-mobility being determined by the frictional resistance encountered by ions in moving over the molecules of the solution. Aside from this, moreover, there is much direct experimental evidence that conditions which affect the viscosity of the medium affect in an approximately inverse proportion. This is most clearly shown in the case of temperature, the effects of which on the viscosity of water and on the

¹ Z. physik. Chem., 9, 495 (1892).

mobility of ions in dilute aqueous solution are approximately the same.¹ Thus multiplying the viscosities of water at 0° and 18° by the respective means of the conductance values² for the univalent ions K⁺, Na⁺, Ag⁺, Cl⁻, NO₃⁻, ClO₃⁻, the following results are obtained:

$$\text{At } 0^\circ: \eta_0 \Lambda_0 = 0.01793 \times 35.17 = 0.630.$$

$$\text{At } 18^\circ: \eta_0 \Lambda_0 = 0.01052 \times 57.18 = 0.604.$$

Furthermore, it has been shown³ that for five uni-univalent salts investigated at 18°, 100°, and 156° the values of $\eta_0 \Lambda_0$ are:

$$\text{At } 18^\circ: \eta_0 \Lambda_0 = 0.01052 \times 113 = 1.19.$$

$$\text{At } 100^\circ: \eta_0 \Lambda_0 = 0.00283 \times 369 = 1.04.$$

$$\text{At } 156^\circ: \eta_0 \Lambda_0 = 0.00179 \times 566 = 1.01.$$

The form of the viscosity correction has recently been discussed in detail by Washburn.⁴ Upon the basis of the relation between the changes in ion-mobility and viscosity produced (1) by change of temperature (as calculated by Johnston⁵), (2) by the addition of non-electrolyte (as shown by the experiments of Green⁶), and (3) by dissolving the same salt in separate solvents (as shown by the experiments of Dutoit and Duperthuis⁷), Washburn suggests for calculating ionization the equation

$$r = \frac{\Lambda}{\Lambda_0} \left(\frac{\eta}{\eta_0} \right)^m. \quad (31)$$

He shows that the value of m never differs from unity by more than 0.2, and that the ionization values up to 0.5 normal calculated by equations (30) and (31) differ in the cases cited by him by only 2%, while those calculated by (29) and (30) differ by nearly 9% of their values.

The existing evidence may therefore be said to lead to the conclusion that, so far as the viscosity correction is concerned, the ratio $\Lambda\eta/\Lambda_0\eta_0$ furnishes a much closer approximation to the true ionization values than the ratio Λ/Λ_0 and one sufficiently close for most salts up to moderate concentrations, such as 0.5 normal; but that equation (31) gives a still closer approximation.

Throughout this article the ratio $\Lambda\eta/\Lambda_0\eta_0$ will be employed as a measure of ionization, because of its greater simplicity and because at the higher concentrations, where equation (31) would give an appreciably different result, other factors doubtless influence the ionization values to a far greater extent.

Entirely aside from physical effects which may cause the mobility of

¹ Cf. Kohlrausch, *Proc. Roy. Soc.*, 71, 383 (1903).

² For the ion-conductances at 18° see Table XIII of this article; for those at 0° see Johnston, *THIS JOURNAL*, 31, 1015 (1909).

³ *THIS JOURNAL*, 30, 342 (1908).

⁴ *Ibid.*, 33, 1464-1474 (1911).

⁵ *Ibid.*, 31, 1010 (1909).

⁶ *J. Chem. Soc.*, 93, 2049 (1908).

⁷ *J. chim. phys.*, 6, 726 (1908).

the ions to vary with increasing concentration, the calculation of ionization from the conductance ratio or the conductance-viscosity ratio may lose its significance owing to changes in the chemical composition of the ions.

Of such possible changes the simplest is a decrease in the hydration of the ions with increasing concentration, whereby their mobility would presumably be increased. Such a change doubtless takes place in many cases at high concentration, but probably to an important extent only after the chemical activity of the water in the solution has become substantially different from that of pure water. Now the vapor pressure is a measure of the active mass¹ or activity² of the solvent; and Raoult's law gives for the ratio of the vapor pressure of solution and pure solvent the expression $p/p_0 = N_0/(N_0 + iN)$, where N_0 and N are the numbers of mols of solvent and solute, respectively, and i is the mol-number of the solute. Using the mean values of i given for the uni-univalent salts in the first paper of this series,³ the values p/p_0 at concentrations between 0.05 and 0.5 normal are found to be as follows:

Concentration.....	0.05	0.1	0.2	0.5
p/p_0	0.998	0.997	0.993	0.984

It will be seen that the change in activity of the water begins to be considerable at 0.1 normal, and that it becomes much larger at the higher concentrations. In the case of ions which form relatively unstable hydrates (that is, such as are in a state of partial dissociation), it may therefore be expected that the mobility will increase fairly rapidly above 0.1 normal.

A second important chemical change, also involving the solvent, is hydrolysis, which takes place especially in the case of salts of weak acids or bases. This, even when relatively small, is likely to influence seriously the determination of the Λ_0 value. It is therefore desirable to note the relation between hydrolysis at different concentrations and the ionization constant K_A or K_B of the weak acid or base which may be involved. The following table shows the percentage hydrolysis ($100h$) calculated by the approximate mass-action equation $\frac{h^2}{1-h} = \frac{K_w}{C K_{A \text{ or } B}}$ for salts of a slightly ionized acid (or base) and a nearly completely ionized base (or acid) at 25° (where the ionization constant of water K_w is 10^{-14}).

K_A or K_B .	10^{-4} .	10^{-5} .	10^{-6} .	10^{-7} .	10^{-8} .
0.1 N.....	0.0032	0.0100	0.0316	0.100	0.316
0.01 N.....	0.0100	0.0316	0.100	0.316	0.995
0.001 N.....	0.0316	0.100	0.316	0.995	3.11
0.0001 N.....	0.100	0.316	0.995	3.11	9.51

¹ See Nernst, "Theoretische Chemie," 4th Ed., pp. 457, 633 (1903).

² Lewis, *Proc. Amer. Acad.*, 43, 279 (1907).

³ THIS JOURNAL, 32, 1027 (1910).

In the case of salts of the uni-bivalent type or of a higher valence type, if, as seems *a priori* probable, the intermediate ion is present in considerable proportion, the conductance ratio or conductance-viscosity ratio must lose its significance as an exact measure of ionization, even at fairly small concentrations. Thus if a salt B_2A is ionized to an extent γ_1 into B^+ and BA^- , and to an extent γ_2 into $2B^+$ and A^{2-} , we have

$$\frac{\Lambda}{\Lambda_0} = \frac{\gamma_2(\Lambda_{B^+} + \Lambda_{A^{2-}}) + \frac{1}{2}\gamma_1(\Lambda_{B^+} + \Lambda_{BA^-})}{\Lambda_{B^+} + \Lambda_{A^{2-}}}; \quad (32)$$

or

$$\gamma = \gamma_2 + \frac{1}{2}\gamma_1 \frac{\Lambda_{B^+} + \Lambda_{BA^-}}{\Lambda_{B^+} + \Lambda_{A^{2-}}}. \quad (33)$$

The factor in the last term by which $\frac{1}{2}\gamma_1$ is multiplied is probably always considerably less than unity, since BA^- is an ion of smaller valence and of greater complexity than A^{2-} . Therefore, since the equivalent concentrations (C_{B^+} and $C_{A^{2-}}$) of the ions B^+ and A^{2-} are really equal to the equivalent concentration C of the salt multiplied by $\gamma_2 + \frac{1}{2}\gamma_1$, and by γ_2 , respectively, C_{B^+} will evidently be found somewhat too small and $C_{A^{2-}}$ somewhat too large if calculated in the usual way by multiplying C by Λ/Λ_0 .

Throughout this article, however, the ratio Λ/Λ_0 , or at the higher concentrations the ratio $\Lambda\eta/\Lambda_0\eta_0$, will be called the *ionization*, it being understood that it has the theoretical significance which this word properly denotes only when none of the complicating factors which have been discussed in the preceding paragraphs come into consideration.

12. The Conductance and Viscosity Data.

In the preceding papers on freezing point and transference, the attempt was made to summarize all the existing data that seemed to be fairly accurate. The experimental material relating to conductance is, however, so extensive that a complete presentation of it seems superfluous. From the available data a selection has therefore been made with the view only of bringing together enough of the best results thus far attained to furnish adequate material for the discussion of the theoretical relations, which forms the main purpose of this series of articles. At 18° all the data published since 1898 by Kohlrausch and his associates have been reproduced, as well as those obtained by the workers in this laboratory; in addition, the results of Wershoven on the cadmium salts, and a few other results of special interest, have been included. At 25° only such data have been used as seem most suitable for determining the equivalent conductances of the separate ions at that temperature. At 0° the data have been selected with the ideas of furnishing the material for calculating the change of ionization between 0° and 18° and the ionization at 0° of those salts whose freezing points have been determined.

The following tables contain the experimental values of the equivalent conductance, expressed in reciprocal ohms per equivalent per cubic centimeter, Kohlrausch's values being corrected so as to conform to the international atomic weights for 1911. Tables VIII and X have been divided for convenience into two parts: the first part includes the data for the concentrations from 0 to 5 millinormal, up to which the viscosity of the solution is, with the few exceptions noted, identical with that of water within 0.1%; the second part includes the data for the higher concentrations, the equivalent conductance Λ being always given for each salt in the first row, the viscosity ratio η/η_0 (represented in the tables by η) being given in the second row, and the product of the conductance by the viscosity ratio $\Lambda\eta/\eta_0$ being given in the third row. The figures within parentheses following the formula of the salt refer to the notes at the end of the tables, which show the source from which the data in the same row were obtained.

TABLE VIIIa.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 18° AT CONCENTRATIONS 0 TO 5 MILLI-EQUIVALENTS PER LITER.

Concentration.....	0.	0.1.	0.2.	0.5.	1.	2.	5.
NaCl (1)...	108.9	108.03	107.75	107.11	106.42	105.48	103.71
KCl (1)...	130.0	129.00	128.70	128.04	127.27	126.24	124.34
LiCl (1)...	98.8	97.96	97.67	97.01	96.34	95.44	93.75
RbCl (3)...	133.0	132.3	130.3
CsCl (3)...	133.5	132.2	131.9	131.24	130.54	129.38	127.33
TlCl (3)...	131.4	130.33	130.00	129.18	128.23	126.81	123.73
NH ₄ Cl (7a)...	130.2	126.5
KBr (3)...	132.2	131.05	130.76	130.05	129.28	128.22	126.31
KI (3)...	131.1	129.76	129.50	128.97	128.25	127.21	125.33
KSCN (3)...	121.2	120.13	119.93	119.29	118.55	117.57	115.73
KF (3)...	111.2	110.37	110.13	109.48	108.80	107.82	106.07
NaF (3)...	90.1	89.24	88.95	88.39	87.76	86.89	85.17
TlF (3)...	112.6	114.38	114.64	114.45	113.25	111.29	108.18
NaNO ₃ (1)...	105.2	104.45	104.09	103.53	102.75	101.80	99.97
KNO ₃ (1)...	126.3	125.40	125.08	124.34	123.55	122.50	120.38
LiNO ₃ (1)...	95.1	94.30	93.99	93.36	92.71	91.81	$\left\{ \begin{array}{l} 90.18 \\ 90.3^* \end{array} \right.$
TlNO ₃ (3)...	127.7	126.63	126.30	125.61	124.70	123.48	121.11
AgNO ₃ (3)...	115.8	115.01	114.56	113.88	113.14	112.07	110.03
KClO ₃ (3)...	119.6	118.63	118.35	117.68	116.92	115.84	113.84
KBrO ₃ (5)...	112.1	109.9	108.7	106.9
NaIO ₃ (2)...	77.4	76.69	76.44	75.83	75.19	74.30	72.62
KIO ₃ (2)...	98.5	97.64	97.34	96.72	96.04	95.04	93.2
LiIO ₃ (2)...	67.3	66.66	66.43	65.87	65.27	$\left\{ \begin{array}{l} 64.43 \\ 64.5^* \end{array} \right.$	$\left\{ \begin{array}{l} 62.89 \\ 63.0^* \end{array} \right.$
HCl (6)...	380.0	378.1	377.8	377.0	375.9	375.3	372.6
HNO ₃ (6)...	376.5	373.9	372.9	371.4
BaCl ₂ (4)...	120.9	117.01	115.60
CaCl ₂ (4)...	117.4	115.17	114.55	113.34	111.96	110.07	$\left\{ \begin{array}{l} 106.70 \\ 106.8^* \end{array} \right.$

* Corrected for viscosity.

TABLE VIIIa (continued).

Concentration.....		0.	0.1.	0.2.	0.5.	1.	2.	5.
MgCl ₂	(4)...	111.4	109.43	108.87	107.68	106.35	$\left\{ \begin{array}{l} 104.52 \\ 104.6^* \end{array} \right.$	$\left\{ \begin{array}{l} 101.30 \\ 101.4^* \end{array} \right.$
PbCl ₂	(5)...	126.3	119.15	115.8	109.2
CdCl ₂	(8)...	111.9	104.2	99.7	89.9
CdBr ₂	(8)...	114.1	102.3	97.9	85.5
CdI ₂	(8)...	113.0	97.5	91.4	76.3
Ba(NO ₃) ₂	(4)...	117.2	115.32	114.65	113.30	111.72	109.50	105.29
Sr(NO ₃) ₂	(4)...	113.7	111.74	111.07	109.76	108.31	106.35	102.74
Ca(NO ₃) ₂	(4)...	113.7	111.91	111.19	109.93	108.49	106.54	103.07
Mg(NO ₃) ₂	(5)...	107.7	102.6	100.8	97.7
Cd(NO ₃) ₂	(8)...	108.2	107.8	105.4	99.2
Pb(NO ₃) ₂	(4)...	122.6	120.73	119.94	118.08	116.13	113.54	108.68
Ba(BrO ₃) ₂	(5)...	103.0	97.5	95.5	91.9
K ₂ SO ₄	(4)...	133.0	130.7	130.0	128.5	126.9	124.6	120.3
Na ₂ SO ₄	(9)...	111.9	109.3	108.3	106.7	105.1	103.5	99.8
Li ₂ SO ₄	(4)...	101.8	97.71	96.27
Tl ₂ SO ₄	(5)...	134.4	127.35	124.2	118.4
Ag ₂ SO ₄	(5)...	122.5	116.3	113.6	108.4
K ₂ C ₂ O ₄	(4)...	127.5	125.09	124.83	123.82	122.43	120.46	116.73
MgSO ₄	(4)...	114.4	109.90	108.07	104.21	99.89	$\left\{ \begin{array}{l} 94.14 \\ 94.2^* \end{array} \right.$	$\left\{ \begin{array}{l} 84.53 \\ 84.7^* \end{array} \right.$
ZnSO ₄	(4)...	115.5	109.7	107.7	103.5	98.6	$\left\{ \begin{array}{l} 92.2 \\ 92.3^* \end{array} \right.$	$\left\{ \begin{array}{l} 81.9 \\ 82.0^* \end{array} \right.$
CdSO ₄	(4)...	114.9	109.84	107.60	102.93	97.72	90.92	79.70
CuSO ₄	(4)...	114.4	109.95	107.95	103.56	98.56	$\left\{ \begin{array}{l} 91.94 \\ 92.0^* \end{array} \right.$	$\left\{ \begin{array}{l} 80.98 \\ 81.1^* \end{array} \right.$
MgC ₂ O ₄	(4)...	109.0	94.5	87.0	74.5	63.4	51.4	38.2
K ₄ Fe(CN) ₆	(11)...	159.5	137.0
Ca ₂ Fe(CN) ₆	(11)...	147.0	75.5
La(NO ₃) ₃	(11)...	122.8	110.8
La ₂ (SO ₄) ₃	(11)...	129.5	60.1
K ₂ C ₆ H ₅ O ₇	(11)...	124.6	120.1	115.4	109.9

The Λ_0 values at 18°, given in the tables, were obtained as follows: For the uni-univalent salts for which Kohlrausch gives accurate results, the values of Λ_0 given by him¹ have been adopted (after correcting them for the change in atomic weights). For the remaining uni-univalent substances and for the salts belonging to higher types, the Λ_0 values were found by the graphical method commonly employed in this laboratory, which consists in plotting the values of $1/\Lambda$ for concentrations up to 0.02 normal as abscissas against those of $(C\Lambda)^{n-1}$ as ordinates, the values of $(n-1)$ being varied until a straight line is obtained (or as nearly a straight line as possible); and reading from this plot by extrapolation to $C\Lambda^* = 0$, the value of $1/\Lambda_0$.

The Λ_0 values at 0° were also obtained by the same extrapolation

* Corrected for viscosity.

¹ See Landolt-Börnstein-Meyerhoffer's Tabellen, p. 744.

TABLE VIIIb.—VALUES OF THE CONDUCTANCE, VISCOSITY, AND THE CONDUCTANCE-VISCOSITY PRODUCT AT 18° AT CONCENTRATIONS 10 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....	10.	20.	50.	100.	200.	500.	1000.
NaCl	Δ (1).....	101.88	99.55	95.66	91.96	87.67	80.89
"	η (23).....	(1.0009)	(1.0018)	1.0046	1.0086	1.0167	1.041
"	$\Delta\eta$	101.97	99.73	96.10	92.75	89.13	84.21
KCl	Δ (1).....	122.37	119.90	115.69	111.97	107.90	102.36
"	η (23).....	(0.9996)	(0.9991)	0.9982	0.9959	0.9898
"	$\Delta\eta$	122.37	119.9	115.6	111.8	107.5	101.3
LiCl	Δ (1).....	91.97	89.75	85.97	82.28	77.80	70.60
"	η (23).....	(1.0016)	(1.0032)	(1.0080)	1.0161	1.031	1.072
"	$\Delta\eta$	92.1	90.0	86.7	83.6	80.2	75.7
RbCl	Δ (3).....	125.3	113.9	101.9
"	η (21).....	(0.998)	(0.976)
"	$\Delta\eta$	125.3	113.7	99.5
CsCl	Δ (3).....	125.07	113.44
"	η (21).....	(0.997)
"	$\Delta\eta$	125.07	113.1
TlCl	Δ (3).....	120.21
NH ₄ Cl	Δ (7a).....	122.5	118.1 ¹
KBr	Δ (3).....	124.31	121.78	117.69	114.14	110.32	105.30
"	η (20).....	(0.9995)	(0.9989)	(0.9973)	(0.9946)	(0.9893)	(0.9623)
"	$\Delta\eta$	124.3	121.7	117.4	113.5	109.1	101.3
KI	Δ (3).....	123.44	121.10	117.26	113.98	106.2
"	η (23).....	(0.9992)	(0.9983)	(0.9955)	0.9908	0.9551
"	$\Delta\eta$	123.3	120.9	116.7	112.9	101.4
KSCN	Δ (3).....	113.87	111.51	107.67	104.21	95.63
KF	Δ (3).....	104.19	101.78	97.65	93.94	82.0

¹ At 30 millinormal.

TABLE VIIIb (continued).

Concentration.....	10.	20.	50.	100.	200.	500.	1000.
NaF	A (3).....	81.0	76.94	73.06	67.9	59.9	51.9
TiF	A (3).....	102.22	97.38	92.61	78.78	71.54
NaNO ₂	A (1).....	95.57	91.35	87.16	82.21	73.99	65.81
"	η (23).....	(1.0005)	1.0023	1.0044	1.0082	1.0219	1.054
"	Aη	95.7	91.6	87.5	82.9	75.6	69.4
KNO ₃	A (1).....	115.12	109.78	104.71	98.67	89.18	80.41
"	η (23).....	(0.9989)	0.9972	0.9941	0.9883	0.9745	0.962
"	Aη	115.0	109.5	104.1	97.5	86.9	77.4
LiNO ₃	A (1).....	86.27	82.58	79.06	74.89	67.88	60.69
"	η (23).....	(1.0033)	1.0062	1.0112	1.020	1.0503	1.102
"	Aη	86.6	83.1	79.9	76.4	71.3	66.9
TiNO ₃	A (3).....	107.93	101.19
"	η	(0.997) ¹	(0.994) ¹
"	Aη	107.6	100.6
AgNO ₃	A (3).....	105.1	99.50	94.33	77.5	67.6
"	η (21).....	1.020	1.057
"	Aη	105.1	99.50	94.33	79.1	71.5
KClO ₃	A (3).....	108.81	103.74	99.19	93.73	85.28
"	η (22).....	(0.999)	(0.997)	(0.995)	(0.986)
"	Aη	108.81	103.6	98.9	93.3	84.1
KBrO ₃	A (5).....	102.0	97.3	93.0	87.8
NaIO ₃	A (2).....	68.56	64.43	60.46	55.45
"	η (23).....	(1.005)	(1.012)	(1.025)	1.050
"	Aη	68.9	65.2	62.0	58.2
KIO ₃	A (2).....	88.64	84.06	79.67	74.34
"	η (23).....	(1.0027)	(1.0067)	(1.0134)	1.0270
"	Aη	88.9	84.7	80.7	76.3

LiIO ₃	<i>A</i>	(2)	61.23	59.05	55.26	51.50	46.88	38.98	31.21
"	<i>η</i>	(23)	(1.003)	(1.006)	(1.016)	1.031	1.062	(1.178)	1.388
"	<i>Aη</i>		61.4	59.4	56.1	53.1	49.8	45.9	43.3
HCl	<i>A</i>	(6)	369.3	365.5	358.4	351.4
HNO ₃	<i>A</i>	(7)	365.0	353.7	346.4
BaCl ₂	<i>A</i>	(4)	106.67	102.53	96.04	90.78	85.18	77.29	70.14
"	<i>η</i>	(18)	(1.001)	(1.002)	(1.005)	(1.011)	(1.021)	(1.052)	1.107
"	<i>Aη</i>		106.8	102.7	96.5	91.8	87.0	81.3	77.6
CaCl ₂	<i>A</i>	(4)	103.37	99.38	93.29	88.19	82.79	74.92	67.54
"	<i>η</i>	(23)	(1.0017)	(1.0033)	(1.0083)	1.0167	(1.0306)	1.0751	1.1501
"	<i>Aη</i>		103.6	99.7	94.1	89.7	85.3	80.5	77.7
MgCl ₂	<i>A</i>	(4)	98.14	94.33	88.47	83.42	77.84	69.50	61.45
"	<i>η</i>	(23)	(1.0023)	(1.0051)	(1.0116)	(1.0209)	1.0423	(1.101)	1.213
"	<i>Aη</i>		98.4	94.8	89.5	85.2	81.1	76.5	74.5
PbCl ₂	<i>A</i>	(5)	102.1	93.2	79.2
CdCl ₂	<i>A</i>	(8)	82.2	74.2	62.1	50.1	41.0	30.4	21.4
"	<i>η</i>	(21)	(1.002)	(1.006)	(1.012)	(1.025)	(1.063)	(1.134)
"	<i>Aη</i>		82.2	74.3	62.5	50.7	42.0	32.3	24.3
CdBr ₂	<i>A</i>	(8)	75.4	65.4	51.7	43.0	34.8	24.9	17.9
CdI ₂	<i>A</i>	(8)	64.8	53.0	39.0	29.5	23.3	18.1	15.1
Ba(NO ₃) ₂	<i>A</i>	(4)	100.96	95.66	86.81	78.94	70.18	56.60
"	<i>η</i>	(21)	1.002	1.004	1.008	1.017	1.044
"	<i>Aη</i>		100.96	95.9	87.2	79.6	71.4	59.1
Sr(NO ₃) ₂	<i>A</i>	(4)	99.04	94.52	87.30	80.93	73.80	62.72	52.07
"	<i>η</i>	(21)	1.002	1.004	1.009	1.019	1.049	1.115
"	<i>Aη</i>		99.04	94.7	87.6	81.7	75.2	65.8	58.1
Ca(NO ₃) ₂	<i>A</i>	(4)	99.53	95.18	88.41	82.48	75.94	65.70	55.86
"	<i>η</i>	(21)	1.001	1.002	1.004	1.008	1.017	1.053	1.117
"	<i>Aη</i>		99.6	95.3	88.8	83.1	77.2	69.2	62.4

¹ Assumed to be identical with the values for KNO₃.

TABLE VIIIb (continued).

Concentration.....	10.	20.	50.	100.	200.	500.	1000.
Mg(NO ₃) ₂	Δ (5).....	90.9	85.3	80.5	75.3
"	η (21).....	1.003	1.008	1.016	1.032
"	Δη	91.2	86.0	81.8	77.7
Cd(NO ₃) ₂	Δ (8).....	91.4	85.1	77.9	71.8	63.2	53.6
"	η (21).....	1.003	1.007	1.015	1.031	1.074	1.165
"	Δη	91.7	85.7	79.1	74.0	67.9	62.4
Pb(NO ₃) ₂	Δ (4).....	97.01	86.38	77.27	67.36	53.21	42.02
"	η (23).....	(1.0017)	(1.0043)	1.0087	1.0166	1.044	1.100
"	Δη	97.2	86.8	77.9	68.5	55.6	46.2
Ba(BrO ₃) ₂	Δ (5).....	83.6
K ₂ SO ₄	Δ (4).....	110.3	101.9	94.9	87.7	78.4	71.6
"	η (23).....	(1.0033)	(1.0060)	1.0111	(1.021)	(1.049)	1.101
"	Δη	110.7	102.5	96.0	89.5	82.2	78.8
Na ₂ SO ₄	Δ (9)(10).....	83.64	77.07	69.95
"	η (18).....	(1.011)	(1.022)	(1.044)
"	Δη	84.6	78.8	73.0
Li ₂ SO ₄	Δ (4).....	82.06	74.59	68.07	60.97	50.45	41.31
"	η (23).....	(1.0065)	1.015	1.029	1.057	1.143	1.303
"	Δη	82.6	75.7	70.0	64.4	57.7	53.8
Tl ₂ SO ₄	Δ (5).....	104.55	92.7	83.1	73.8
"	η	1.0033 ¹	1.0060 ¹	1.0111 ¹	1.021 ¹
"	Δη	104.9	93.3	84.0	75.4
Ag ₂ SO ₄	Δ (5).....	96.1
K ₂ C ₂ O ₄	Δ (4).....	108.07	100.77	94.79	88.57	73.63
"	η (23).....	(1.0025)	(1.0063)	1.0127	1.0236	1.113
"	Δη	108.3	101.4	96.0	90.7	82.0
H ₂ SO ₄	Δ (7).....	253.5	233.3

MgSO ₄	A (4).....	76.21	67.68	56.92	49.68	43.19	28.91
"	η (23).....	(1.0039)	1.0077	1.0181	1.034	1.068	1.381
"	Δη	76.5	68.2	57.9	51.4	46.1	39.9
ZnSO ₄	A (4).....	72.9	63.8	52.8	45.4	39.1	26.2
"	η (18).....	(1.003)	(1.006)	(1.016)	(1.031)	(1.064)	1.362
"	Δη	73.1	64.2	53.6	46.8	41.6	35.7
CdSO ₄	A (4).....	70.34	60.95	49.60	42.21	35.89	28.74	25.58
"	η (21).....	1.002	1.005	1.013	1.026	1.061	1.157	1.347
"	Δη	70.5	61.3	50.2	43.3	38.1	33.3	31.8
CuSO ₄	A (4).....	71.74	62.40	51.16	43.85	37.66	25.77
"	η (18).....	(1.004)	(1.008)	(1.016)	(1.032)	(1.064)	1.371
"	Δη	72.0	62.9	52.0	45.3	40.1	35.3
MgC ₂ O ₄	A (4).....	29.6	23.0	16.4	12.7	10.0
C = 12.5								
K ₄ Fe(CN) ₆	A (11).....	113.4	93.7	84.9	77.8
"	η (20).....	(1.001)	(1.005)	(1.011)	(1.021)
"	Δη	113.5	94.2	85.8	79.4
Ca ₂ Fe(CN) ₆	A (11).....	49.9	38.5	35.1	32.9
La(NO ₃) ₃	A (11).....	98.5	86.1	79.4	72.1
La ₂ (SO ₄) ₃	A (11).....	37.4	25.7	21.4	17.8
K ₂ C ₂ H ₂ O ₇	A (11).....	101.8	87.8	80.8

¹ Assumed to be identical with the values for K₂SO₄.

TABLE IXa.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 0° AT CONCENTRATIONS 0 TO 12.5 MILLI-EQUIVALENTS PER LITER.

Concentration.....	0.	0.5.	1.	2.	5.	10.	12.5.
KCl (17).....	82.0	80.3	77.6
" (13).....	82.0	80.9	80.4	79.7	78.6	77.4
" (12) ¹	81.4	80.3	80.0	79.6	78.7	77.6
" (24).....	81.0
NaCl (17).....	67.6	65.9	63.3
" (13).....	67.2	65.5	63.3	61.7
LiCl (24).....	60.3
KI (17).....	83.5	81.8
NaNO ₃ (17).....	66.1	64.7	61.7
" (13).....	65.1	64.4	63.4	61.9	60.4
KNO ₃ (17).....	81.1	79.3	75.7
" (13).....	80.8	77.8	77.1	76.1	74.6	73.1
" (11).....	78.6	75.3
CsNO ₃ (24).....	84.0
AgNO ₃ (17).....	73.3	71.6	68.3
" (13).....	(71.8)	70.7	70.2	69.6	68.4	67.1
KClO ₃ (13).....	(74.2)	72.5	71.9	71.2	70.0	68.8
BaCl ₂ (17).....	75.2	71.9	66.3
" (12) ²	75.5	73.1	72.3	71.1	69.0	66.9
" (13).....	72.8	68.7	65.3
Ba(NO ₃) ₂ (17).....	73.6	70.3	63.3
" (13).....	(71.0)	68.8	67.8	66.4	64.0	61.6
Sr(NO ₃) ₂ (13).....	69.1	67.0	66.0	64.6	62.3	60.2
Ca(NO ₃) ₂ (11).....	66.5	61.6
K ₂ SO ₄ (13).....	78.2	77.0	75.6	73.2	70.8
" (17).....	83.2	79.0	72.4
Na ₂ SO ₄ (17).....	68.5	64.2	58.5
K ₂ C ₂ O ₄ (11).....	74.9	69.3
MgSO ₄ (17).....	68.9	60.5	46.6
" (12) ³	70.7	63.9	61.4	(57.9)	51.2	46.8
" (13) ⁴	(69.0)	63.3	60.3	56.6	50.9	46.3
CuSO ₄ (12) ⁵	70.7	63.3	60.2	56.3	50.0	44.5
" (13) ⁶	(70.7)	63.0	60.0	56.3	50.1	44.8
ZnSO ₄ (13).....	(70.0)	63.6	60.3	56.4	50.4	45.4
CdSO ₄ (13).....	(69.0)	61.6	58.7	55.1	49.0	43.7
La(NO ₃) ₃ (11).....	68.9	61.4
K ₂ C ₈ H ₅ O ₇ (11).....	71.0	67.6	62.9

¹ 80.6 for C = 0.2 and 0.1.² 73.9 for C = 0.2; 74.2 for C = 0.1.³ 66.3 for C = 0.2; 67.6 for C = 0.1. The result for C = 2 is incorrect, as shown by the plot.⁴ 66.6 for C = 0.2; 68.6 for C = 0.1.⁵ 66.0 for C = 0.2; 67.4 for C = 0.1.⁶ 65.9 for C = 0.2; 67.6 for C = 0.1.

TABLE IXa (continued).

Concentration.....	0.	0.5.	1.	2.	5.	10.	12.5.
$K_4Fe(CN)_6$ (11).....	98.4	91.6	84.8	71.0
$La_2(SO_4)_3$ (11).....	39.8	24.9
$Ca_2Fe(CN)_6$ (11).....	47.1	31.2
" (14).....	60.0	52.6	45.3	37.1	31.8
$Sr_2Fe(CN)_6$ (14).....	60.3	52.5	44.9	36.8	31.9
$KMnO_4$ (12) ¹	75.9	75.5	75.1	74.6	73.5	72.2
$K_2Fe(CN)_6$ (12) ²	97.4	92.8	91.1	88.7	84.6	80.5

TABLE IXb.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 0° AT CONCENTRATIONS 20 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....	20.	50.	100.	200.	500.	1000.
KCl (17).....	73.7
" (13).....	76.0	73.7	71.7	69.7	67.2	65.6
" (12).....	76.1	74.0
" (24).....	73.9	71.5	69.1	66.6
NaCl (17).....	59.6
" (13).....	60.2	58.2	56.3	54.0	50.8	47.4
LiCl (24).....	53.0	51.1	48.4	44.0
KI (17).....	75.3
$NaNO_3$ (17).....	57.8
" (13).....	58.7	55.9	53.4	51.1	48.0	46.5
KNO_3 (17).....	70.5
" (13).....	71.1	68.0	65.1	61.7	56.5	52.1
" (11).....	70.7	67.2
$CsNO_3$ (24).....	72.9	69.3	65.2	59.3
$AgNO_3$ (17).....	63.1
" (13).....	65.4	61.8	57.6	53.1	47.9	44.5
$KClO_3$ (13).....	67.2	64.2	61.1	56.9
$BaCl_2$ (17).....	60.0
" (12).....	64.5	60.7
" (13).....	61.9	57.9	54.8	51.6	47.0	44.0
$Ba(NO_3)_2$ (17).....	54.2
" (13).....	58.4	52.2	47.0	42.8
$Sr(NO_3)_2$ (13).....	57.4	53.0	49.1	44.6	38.4	32.1
$Ca(NO_3)_2$ (11).....	55.6	51.9	48.3
K_2SO_4 (17).....	63.7
" (13).....	67.7	62.7	58.5	52.0	48.4
Na_2SO_4 (17).....	51.2

¹ These results are given in arbitrary conductance units. Additional values are 75.5 for $C = 0.2$; 75.6 for $C = 0.1$.

² These results are given in arbitrary conductance units. Additional values are 94.3 for $C = 0.2$; 95.1 for $C = 0.1$.

TABLE IXb (continued).

Concentration.....		20.	50.	100.	200.	500.	1000.
K ₂ C ₂ O ₄	(11).....	63.0	59.3	55.8
MgSO ₄	(17).....	35.0
"	(12).....	41.7	35.3	30.9	27.0	22.3
"	(13).....	41.6	35.2	30.8	26.5	21.2	17.6
CuSO ₄	(12).....	38.8	32.6	28.2	24.3	19.1	15.9
"	(13).....	39.1	32.3	27.7	23.6	19.0	15.9
ZnSO ₄	(13).....	40.1	33.7	29.6	25.7	21.7	16.3
CdSO ₄	(13).....	38.1	31.1	26.2	22.4	18.3	15.0
La(NO ₃) ₃	(11).....	54.0	49.9	46.0
K ₂ C ₂ H ₂ O ₇	(11).....	54.4	50.2	43.5
K ₄ Fe(CN) ₆	(11).....	58.2	53.0	48.8
La ₂ (SO ₄) ₃	(11).....	17.2	14.4	12.1
Ca ₂ Fe(CN) ₆	(11).....	24.1	21.9	20.6
"	(14).....	27.4	23.3	21.2	20.0	19.0	18.4
Sr ₂ Fe(CN) ₆	(14).....	28.0	24.1	21.6	20.0	18.4	17.2
KMnO ₄	(12).....	70.6

TABLE Xa.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 25° AT CONCENTRATIONS 0 TO 5 MILLI-EQUIVALENTS PER LITER.

Concentration.....		0.	0.2	0.5	1.	2.	5.
NaCl	(15)(5).....	127.0	124.1	123.05	121.0
KCl	(15).....	150.6	146.55	143.95
KI	(16).....	151.3	147.9	146.7	144.5
KNO ₃	(11).....	145.4	140.7	...
KBrO ₃	(5).....	129.6	126.9	125.6	123.4
HCl	(5).....	426.0	420.4	418.6	415.3
HNO ₃	(7).....	420.0	...	417.0	...	413.7	...
PbCl ₂	(5).....	147.0	138.7	134.5	126.8
Mg(NO ₃) ₂	(5).....	125.6	119.5	117.4	{ 113.7 113.8*
Ca(NO ₃) ₂	(11).....	130.6	123.7	...
Ba(BrO ₃) ₂	(5).....	120.0	113.6	111.2	106.95
K ₂ SO ₄	(15).....	154.8	144.8	139.8
Na ₂ SO ₄	(15).....	131.2	122.3	{ 117.45 117.6*
Tl ₂ SO ₄	(5).....	156.0	147.8	144.2	137.3
Ag ₂ SO ₄	(5).....	143.4	135.7	132.6	126.3
K ₂ C ₂ O ₄	(11).....	147.5	139.2	...
K ₄ Fe(CN) ₆	(15).....	185.0	...	173.1	...	160.1	146.9
Na ₄ Fe(CN) ₆	(15).....	162.0	...	150.7	...	140.5	129.6
Ca ₂ Fe(CN) ₆	(11).....	171.0	86.2	...
La(NO ₃) ₃	(11).....	142.6	128.9	...
La ₂ (SO ₄) ₃	(11).....	152.0	67.9	...
K ₂ C ₂ H ₂ O ₇	(11).....	144.5	..	139.4	...	134.5	128.2

* Corrected for viscosity

TABLE Xb.—VALUES OF THE EQUIVALENT CONDUCTANCE, VISCOSITY, AND CONDUCTANCE-VISCOSITY PRODUCT AT 25° AT THE CONCENTRATIONS 10 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....	10.	20.	50.	100.	200.	500.	1000.
NaCl	A (15)(5).....	118.7	115.9	111.2	106.8	101.7	93.45
"	η (19).....	(1.001)	(1.002)	(1.005)	(1.010)	(1.0191)	1.0471
"	Aη	118.8	116.1	111.8	107.9	103.6	97.9
KCl	A (15).....	141.4	138.65	133.65	129.0	124.2	117.4
"	η (21).....	(0.9994)	(0.9988)	(0.9971)	(0.9942)	(0.9922)	0.9872
"	Aη	141.4	138.5	133.3	128.3	123.2	115.9
KI	A (16).....	142.3	139.4	134.7	130.8
"	η (22).....	(0.9994)	(0.9987)	(0.9967)	(0.9934)
"	Aη	142.2	139.2	134.3	129.9
C = 12.5							
KNO ₃	A (11).....	134.9	126.3	120.3
"	η (21).....	(0.9992)	(0.9968)	(0.9937)
"	Aη	134.8	125.9	119.5
C = 10							
KBrO ₃	A (5).....	121.0	117.8	112.4	107.2	101.1
HCl	A (5).....	411.6	406.7	398.4	390.4	380.2
"	η (19).....	(1.001)	(1.002)	(1.004)	(1.008)	(1.0134)	1.0671
"	Aη	412.0	407.5	400.0	394.4	385.3
HNO ₃	A (7).....	406.0	393.3	385.0
"	η (19).....	(1.0011)	(1.0021)
"	Aη	406.0	393.7	385.8
PbCl ₂	A (5).....	118.2	107.6	91.3
Mg(NO ₃) ₂	A (5).....	110.05	105.7	99.0	93.4	87.2
"	η (21).....	(1.002)	(1.003)	(1.008)	(1.016)	(1.032)
"	Aη	110.3	106.0	99.8	94.9	90.0

TABLE Xb (continued).

Concentration.....	10.	20.	50.	100.	200.	500.	1000.
	C=						
Ca(NO ₃) ₂	A (11).....	102.6	95.8	88.8
"	η (27).....	(1.004)	(1.008)	(1.017)
"	Δη	103.0	96.5	90.3
	C=						
Ba(BrO ₃) ₂	A (5).....	97.3
K ₂ SO ₄	A (15).....	128.1	118.15	109.9	101.4	90.4
"	η (21).....	(1.0013)	(1.0031)	(1.0062)	(1.0165)	1.0486°
"	Δη	128.3	118.5	110.6	103.1	94.8
Na ₂ SO ₄	A (15).....	106.95	97.9	90.1	81.65
"	η (21).....	(1.004)	(1.009)	(1.019)	(1.042)
"	Δη	107.4	98.8	91.8	85.1
Tl ₂ SO ₄	A (5).....	120.9	107.1	96.0	85.0
"	η ¹	(1.0013)	(1.0031)	(1.0062)	(1.0165)
"	Δη	121.1	107.4	96.6	86.4
Ag ₂ SO ₄	A (5).....	111.7
	C=						
K ₂ C ₂ O ₄	A (11).....	116.5	109.5	102.3
	C=						
K ₄ Fe(CN) ₆	A (15).....	123.3	108.3	98.2	89.75
"	η (21).....	(1.002)	(1.005)	(1.009)	(1.018)
"	Δη	123.5	108.8	99.1	91.4
Na ₄ Fe(CN) ₆	A (15).....	110.0	97.0	88.15	80.2
	C=						
Ca ₂ Fe(CN) ₆	A (11).....	44.4	40.2	37.8
La(NO ₃) ₃	A (11).....	99.7	91.8	83.5
La ₂ (SO ₄) ₃	A (11).....	28.7	23.9	19.8
K ₂ C ₆ H ₄ O ₇	A (11).....	102.1	93.9

¹ Assumed to be identical with K₂SO₄.

References to Conductance Data:

- (1) Kohlrausch and Maltby, *Sitz. ber. königl. Preuss. Akad.*, 1899, 665.
- (2) Kohlrausch, *Ibid.*, 1900, 1002.
- (3) Kohlrausch and Steinwehr, *Ibid.*, 1902, 581.
- (4) Kohlrausch and Grüneisen, *Ibid.*, 1904, 1215.

All the values obtained in these four investigations have been corrected so as to conform to the international atomic weights for 1911 in the way suggested by Kohlrausch (*Z. physik. Chem.*, 72, 43 (1909)), assuming when not definitely stated that the official atomic weights for the year in which the article was published were used.

- (5) Hunt, *THIS JOURNAL*, 33, 795 (1911).
- (6) Goodwin and Haskell, *Phys. Review*, 19, 386 (1904).
- (7) Noyes and Eastman, *Carnegie Publ.*, 63, 262. *THIS JOURNAL*, 30, 335 (1908).
- (7a) Sosman, *Carnegie Publ.*, 63, 225 (1908).
- (8) Wershoven, *Z. physik. Chem.*, 5, 481 (1890).

The results on some of the cadmium salts given in this paper were used. The ratio between the units used by Wershoven and those used by Kohlrausch and Steinwehr was obtained by a comparison of their results with potassium iodide, and was found to be 1.064. This ratio gave a satisfactory agreement between the measurements of Wershoven and of Kohlrausch and Grüneisen for cadmium sulfate between $C = 1000$ and $C = 10$ but showed deviations amounting to 1% between $C = 10$ and $C = 2$.

- (9) Archibald, *Proc. N. S. Inst.*, 10, 49, 129.

The results for sodium sulfate at 18° were taken. The correction factor, 1.055, was found to give satisfactory results for potassium sulfate compared with the results of Kohlrausch and Grüneisen.

- (10) Sherrill, *THIS JOURNAL*, 32, 744 (1910).
- (11) Noyes and Johnston, *Ibid.*, 31, 987 (1909).
- (12) Whetham, *Proc. Roy. Soc.*, 71, 332 (1903).
- (13) Kahlenberg, *J. Phys. Chem.*, 5, 339 (1901).

The results at 0° were used. The values of A and C as given were plotted as ordinates and abscissas, and the results for the concentrations desired taken from the curve. No satisfactory curve was obtained for potassium iodide, so it is omitted. The results for FeSO_4 , NiSO_4 , CoSO_4 , and MnSO_4 are also omitted.

- (14) Earl of Berkeley, Hartley and Stephenson, *Trans. Roy. Soc.*, (A) 209, 319 (1909).
- (15) Results obtained by A. C. Melcher in this laboratory not yet published.
- (16) Bray and Mackay, *THIS JOURNAL*, 32, 914 (1910).
- (17) Déguisne, Landolt-Börnstein-Meyerhoffer, *Tabellen*, p. 755 (1905).
- (24) Washburn, *THIS JOURNAL*, 33, 1473 (1911).

References to Viscosity Data:

- (18) Arrhenius, *Z. physik. Chem.*, 1, 284 (1887).
- (19) Reyher, *Ibid.*, 2, 744 (1888).
- (20) Abegg, *Ibid.*, 11, 251 (1893).
- (21) Wagner, *Ibid.*, 5, 31 (1890).
- (22) Sprung, *Pogg. Ann.*, 159, 1 (1876).
- (23) Grüneisen, *Wiss. Abh. der Phys. Tech. Reichsanstalt*, 4, 239 (1905).
- (24) Washburn, *THIS JOURNAL*, 33, 1473 (1911).

method that was used at 18° for those substances for which an apparently accurate series of data was available. Another procedure for obtaining the Λ_0 values at 0° was also employed. This consisted in using the quadratic equations which Kohlrausch¹ derived from the conduc-

¹ *Sitzungsber. königl. Preuss. Akad.*, 1901, 1026.

tance measurements of Déguisne at 2°, 10°, 18°, 16°, and 34°, and which express the Λ_0 values for the salts at various temperatures in terms of the Λ_0 values at 18° and specific temperature coefficients. From them the Λ_0 values given in Table IX opposite the reference number (17) were calculated.

The Λ_0 values for the substances shown in Table X at 25° were obtained in collaboration with Dr. W. C. Bray by plotting the values of $1/\Lambda$ and $(CA)^{-1}$ and extrapolating as already indicated, and also by taking into account the fact that ionizations calculated with them for 25° should not differ materially from ionizations calculated for 18°, for which temperature a reliable series of Λ_0 values is known.

The viscosity data given within parentheses in the tables were derived from the nearest measured value with the aid of the exponential function, $\eta/\eta_0 = k_1C$ or $\log(\eta/\eta_0) = k_2C$, where C is the concentration and k_1 or k_2 is a constant calculated from the measured value. The values given in Table VIIIb were based on measurements at or near 18°, except those of Wagner (reference (21)) which were made at 25°. These values were assumed to be the same at 18° and were used in correcting the conductance values at 18°, except in the case of cesium and rubidium chlorides, whose viscosities were corrected to 18° by means of the same temperature coefficient which potassium and ammonium chlorides have been found to have:

13. Ionization Values at 18°.

TABLE XI.—VALUES OF THE PERCENTAGE IONIZATION ($100 \Lambda\eta/\Lambda_0\eta_0$) AT 18°.

Concentration..	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
NaCl.....	97.7	96.9	95.3	93.6	91.6	88.2	85.2	81.8	77.3	74.1
KCl.....	97.9	97.1	95.6	94.1	92.2	88.9	86.0	82.7	77.9	74.2
LiCl.....	97.5	96.6	94.9	93.2	91.1	87.8	84.6	81.2	76.6	73.7
RbCl.....	98.0	94.2	85.5	74.8
CsCl.....	97.8	96.9	95.4	93.7	84.7
TlCl.....	97.6	96.5	94.2	91.5
KBr.....	97.8	97.0	95.5	94.0	92.1	88.8	85.9	82.5	76.6
KI.....	97.8	97.0	95.6	94.1	92.2	89.0	86.9	77.3	72.7
KSCN.....	97.8	97.0	95.5	94.0	92.0	88.8	86.0
KF.....	97.8	97.0	95.4	93.7	91.5	87.8
NaF.....	97.4	96.4	94.5	92.5	89.9	85.4
TlF.....	96.1	93.6	90.8	86.5
NaNO ₃	97.7	96.8	95.0	93.2	91.0	87.1	83.2	78.8	71.9	66.0
KNO ₃	97.8	97.0	95.3	93.5	91.1	86.7	82.4	77.2	68.8	61.3
LiNO ₃	97.5	96.5	95.0	93.2	91.1	87.4	84.0	80.3	75.0	70.3
TlNO ₃	97.7	96.7	94.8	92.6	84.3	78.8
AgNO ₃	97.7	96.8	95.0	93.1	90.8	85.9	81.4	68.3	61.7
KBrO ₃	98.0	97.0	95.4	93.4	91.0	86.8	83.0
KClO ₃	97.8	96.9	95.2	93.3	91.0	86.6	82.7	78.0	70.3
NaIO ₃	97.1	96.0	93.9	91.7	89.0	84.2	80.1	75.2
KIO ₃	97.5	96.5	94.6	92.8	90.3	86.0	81.9	77.5
LiIO ₃	97.0	95.8	93.6	91.2	88.3	83.4	78.9	74.0	68.2	64.3

TABLE XI (continued).

Concentration..	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
HCl.....	99.0	98.8	98.1	97.2	96.2	94.4	92.5
HNO ₃	99.2	98.7	97.0	94.0	92.1
BaCl ₂	95.6	88.3	85.0	79.8	75.9	72.0	67.2	64.2
CaCl ₂	95.4	93.8	91.0	88.2	84.9	80.2	76.4	72.7	68.6	66.2
MgCl ₂	95.5	93.9	91.0	88.3	85.1	80.3	76.5	72.8	68.7	66.9
PbCl ₂	94.3	91.7	86.5	80.8	73.8	62.7
CdCl ₂	93.1	89.1	80.3	73.5	66.4	55.9	45.3	37.5	28.9	21.7
CdBr ₂	89.7	85.8	74.9	66.1	57.3
CdI ₂	87.0	80.9	67.5	57.3	46.9
Ba(NO ₃) ₂	95.3	93.4	89.8	86.1	81.8	74.4	67.9	60.9	50.4
Sr(NO ₃) ₂	95.3	93.5	90.4	87.1	83.3	77.0	71.9	66.1	57.9	51.1
Ca(NO ₃) ₂	95.4	93.7	90.7	87.6	83.8	78.1	73.1	67.9	60.9	54.9
Mg(NO ₃) ₂	95.3	93.6	90.7	88.0	84.7	79.9	76.0	72.1
Pb(NO ₃) ₂	94.7	92.6	88.6	84.5	79.3	70.8	63.5	55.9	45.4	37.7
Cd(NO ₃) ₂	99.6	97.4	91.7	87.1	84.8	79.2	73.1	68.4	62.8	57.7
Ba(BrO ₃) ₂ ...	94.7	92.7	89.2	85.6	81.2
K ₂ SO ₄	95.4	93.7	90.5	87.2	83.2	77.1	72.2	67.3	61.8	59.2
Na ₂ SO ₄	93.9	92.5	89.3	85.7	75.6	70.4	65.2
Li ₂ SO ₄	94.6	85.4	81.1	74.4	68.8	63.3	56.7	52.8
Tl ₂ SO ₄	94.8	92.4	88.2	83.7	78.0	69.4	62.5	56.1
Ag ₂ SO ₄	94.9	92.7	88.5	84.0	78.4
K ₂ C ₂ O ₄	96.0	94.5	91.6	88.6	84.9	79.5	75.3	71.1	64.3
MgSO ₄	87.3	82.3	74.0	66.9	59.6	50.6	44.9	40.3	34.9
ZnSO ₄	85.4	79.9	71.0	63.3	55.6	46.4	40.5	36.0	30.9
CdSO ₄	85.0	79.1	69.4	61.4	53.4	43.7	37.7	33.2	29.0	27.7
CuSO ₄	86.2	80.4	70.9	62.9	55.0	45.5	39.6	35.1	30.9
MgC ₂ O ₄	58.2	47.2	35.0	27.3
C =				12.5						
K ₄ Fe(CN) ₆	85.9	71.2	59.1	53.8	49.8
La(NO ₃) ₃	90.2	80.2	70.1
K ₂ C ₂ H ₃ O ₇	92.6	88.2	81.7	70.5
La ₂ (SO ₄) ₃	46.4	28.9	19.8
Ca ₂ Fe(CN) ₆	51.4	33.9	26.2

14. Discussion of the Ionization Values at 18°.

A study of the data of Table XI leads to the following conclusions in regard to the relations between the degree of ionization and the chemical composition and valence type of the salts.

1. All the chlorides, bromides, and iodides of all of the alkali elements have, even up to normal concentration, ionization values which are approximately identical, the variations from the average value scarcely ever exceeding 1.5% of that value.

2. The nitrates of the alkali elements and potassium chlorate and bromate form another group for which up to 0.1 normal the ionization values are almost identical (the variations not exceeding 1%).

3. The chlorides of magnesium, calcium, and barium form a third group whose members have within 1% the same ionization up to 0.2 normal.

4. The two acids, hydrochloric and nitric, have also substantially the same ionization values at all concentrations. These are much larger than those for the uni-univalent salts.

5. The average values for these four groups of substances at various equivalent concentrations are as follows:

Conc.....	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
I. M^+X^-	97.8	96.9	95.4	93.8	91.8	88.5	85.5	82.1	77.1	73.9
II. $M^+YO_3^-$	97.8	96.8	95.2	93.3	91.0	86.9	83.1
III. $M^{++}Cl_2^-$...	95.5	93.9	91.0	88.3	85.0	80.1	76.3	72.5
IV. H^+A^-	99.1	98.8	98.1	97.1	96.2	94.2	92.3

6. Of the other uni-univalent salts, potassium sulfocyanate up to 0.1 normal has values conforming to those of Group I; and those for silver nitrate coincide with those of Group II up to 0.02 normal, but become considerably smaller at higher concentrations. Thallous chloride and thallous nitrate have much lower values than the corresponding salts of the alkali elements; thus thallous chloride has a 2.5% lower value at 0.01 normal, and thallous nitrate a 5.5% lower value at 0.1 normal.

7. The nitrates of the univalent elements, and still more markedly, those of the bivalent elements, exhibit a steady decrease in their ionization values, as the atomic weight of the metal increases. Thus at 0.1 normal the values are:

H.	Li.	Na.	K.	Ag.	Cs.	Tl.
92.1	84.0	83.2	82.4	81.4	80.8*	78.8
		Mg.	Ca.	Sr.	Ba.	Pb.
		76.0	73.1	71.9	67.9	63.5

8. In the case of the sulfates the order of decreasing ionization is reversed for the alkali elements, but these have values which are much larger than those for silver and thallium sulfates. Thus at 0.1 and 0.02 normal the values are:

Conc.	K.	Na.	Li.	Ag.	Tl.
0.1	72.2	70.4	68.8	62.5
0.02	83.2	81.7	81.1	78.4	78.0

9. The chlorides and iodates of these univalent metallic elements exhibit differences in the same direction as the sulfates, but of much smaller magnitude.

10. The sulfates of the periodic group embracing magnesium, zinc, and cadmium show decreasing ionization in the order named. Copper sulfate has nearly the same value as zinc sulfate.

11. The ionization values for the salts of the alkali and alkaline earth elements are related to the nature of the anion as shown by the following

* Value at 0°.

grouping—the anions in the same horizontal row having substantially the same influence, and those in any row giving rise to larger ionization than those in the row beneath:

Cl.	Br.	I.	SCN.
NO ₃	ClO ₃	BrO ₃
IO ₃

12. A consideration of all these results shows, however, that in general ionization is not an additive property with respect to the ion-constituents; also that its value is not related to those of the mobilities of the ions.

13. The relation of the ionization value to the valence type of the salt is illustrated by the following figures, which represent the average and limiting values at 18° of the ionization at 0.05 normal and 0.05 formal¹ of the uni-univalent and uni-bivalent salts of the alkali and alkaline earth elements (including magnesium) and of a variety of salts of still higher types.

Valence product.	Ionization at 0.05 normal.			Ionization at 0.05 formal.		
	Average.	Maximum.	Minimum.	Average.	Maximum.	Minimum.
1 × 1	87.0	89.0	83.4	87.0	89.0	83.4
2 × 1	77.8	80.3	74.4 ²	73.1	76.5	67.9
3 × 1	70.3 ³	70.5	70.1	61.0 ³
4 × 1	58.4 ⁴	59.0	57.7	48.8 ⁴	49.8	47.8
5 × 1	40.6 ⁴
2 × 2	46.6 ⁵	50.6	43.7	40.7 ⁵	44.9	37.7

14. The average percentages unionized at 0.05 formal for the different types and the ratio of these to the valence products (v_1v_2) are as follows:

v_1v_2	1 × 1.	2 × 1.	3 × 1.	4 × 1.	5 × 1.	2 × 2.
1— γ	13.0	26.9	39.0	51.2	59.4	59.3
(1— γ)/ v_1v_2	13.0	13.5	13.0	12.8	11.9	14.8

15. Comparison of the Ionization Values at 0° and 18°.

Table XII contains the values of the ratio $100\Lambda/\Lambda_0$ at 18° and 0°. Since its purpose is to show the relative values of the ionization at these two temperatures, and since few viscosity data at 0° are available, the viscosity correction has not been applied at either temperature. This cor-

¹ By 0.05 *formal* is meant a solution containing 0.05 formula-weights of salt per liter of solution.

² Thallous sulfate, lead nitrate and lead chloride have at 0.05 normal the much lower values 69.4, 70.8 and 62.7, respectively.

³ Average for K₃C₆H₅O₇ (potassium citrate) and La(NO₃)₃, uncorrected for viscosity.

⁴ Value for K₄Fe(CN)₆ and for Na₄C₁₁H₂O₁₀ (tetrasodium benzenepentacarboxylate), interpolated from the values of Noyes and Lombard (THIS JOURNAL, 33, 1433 (1911)).

⁵ Value of Na₅C₁₁HO₁₀ pentasodium benzenepentacarboxylate (Noyes and Lombard, *Loc. cit.*).

⁶ Average for MgSO₄, ZnSO₄, CdSO₄, CuSO₄.

TABLE XII.—IONIZATION VALUES AT 0° AND 18° (UNCORRECTED FOR VISCOSITY).

Concentration.	10.	50.	100.	200.	500.
KCl 18°.....	94.1	89.0	86.1	83.0	78.7
" 0° ¹	94.4	89.9	87.3	84.6	81.7
NaCl 18°.....	93.6	87.8
" 0° ²	93.6	88.2
LiCl 18°.....	93.1	87.0	83.3	78.7	71.5
" 0°.....	87.8	84.7	80.2	73.0
KI 18°.....	89.4
" 0°.....	90.2
NaNO ₃ 18°.....	93.2	86.8
" 0° ³	93.3	87.4
KNO ₃ 18°.....	93.5	86.9	82.9
" 0° ⁴	93.3	87.2	82.9
AgNO ₃ 18°.....	93.1	85.9	81.4	66.9
" 0° ⁵	{ 93.5 93.2	86.1 86.1	80.2	74.0	66.7
KClO ₃ 18°.....	93.4	86.7	82.9	78.9
" 0°.....	92.7	86.5	82.3	76.7
BaCl ₂ 18°.....	88.2	79.4
" 0° ⁶	88.6	80.4
Ba(NO ₃) ₂ 18°.....	85.4	74.1	67.4	59.9
" 0°.....	{ 86.8 86.0	73.5 73.6	66.2	60.3
Sr(NO ₃) ₂ 18°.....	87.1	76.8	71.9	66.1	57.9
" 0°.....	87.1	76.7	71.1	64.5	55.6
K ₂ SO ₄ 18°.....	87.1	76.6
" 0° ⁴	87.0	76.6
Na ₂ SO ₄ 18°.....	85.5	74.7
" 0°.....	85.4	74.7
MgSO ₄ 18°.....	66.6	49.8	43.4	37.8
" 0° ⁷	67.1	51.0	44.6	38.4
CuSO ₄ 18°.....	62.7	44.7	38.3	32.9
" 0° ⁸	63.2	45.9	39.5	33.9
C = 12.5					
K ₄ Fe(CN) ₆ 18°.....	71.1	58.7	53.2	48.8
" 0°.....	72.2	59.1	53.9	49.6

¹ Average values of Δ were used with $\Delta_0 = 82.0$.

² Déguisne's results. A satisfactory Δ_0 could not be obtained from Kahlenberg's results.

³ Déguisne's results.

⁴ Results of Déguisne and of Noyes and Johnston. Since Noyes and Johnston's values at 25° agree with those calculated for 25° by Déguisne's equation, the results of Kahlenberg appear to be influenced by some constant error.

⁵ Both series of results were used, each with the Δ_0 value obtained from its own set of measurements. Déguisne's values are in the lower row.

⁶ Whetham's results.

⁷ Kahlenberg's results were used, since these agree better with Déguisne's results for the dilute solutions than do Whetham's.

⁸ Average of Whetham's and Kahlenberg's results.

rection, up to moderate concentrations, cannot, however, be much different at the two temperatures.¹

In studying the change of ionization between 18° and 0°, it has seemed best to eliminate the irregularities arising from experimental errors by finding the average values at 18° and 0° for all of the salts of each valence type given in the table. These averages are as follows:

Equiv. conc.....	10.	50.	100.
Uni-univalent 18°.....	93.4	87.4	83.3
" 0°.....	93.4	87.9	83.5
Uni-bivalent 18°.....	86.7	76.3	69.7
" 0°.....	86.9	76.4	68.7
Bi-bivalent 18°.....	64.7	47.3	40.9
" 0°.....	65.2	48.5	42.1

The differences in the values at 18° and 0° are so small that they do not exceed the probable error. This result shows that ionization values derived from the conductance at 18° may be employed at 0° (for example, in comparisons with those from the freezing-point lowering) without incurring an error greater than that in the determinations at 0°.

16. Equivalent Conductance of the Separate Ions.

Table XIII contains the equivalent conductances of the separate ions at 18° and 25°. The value for the univalent ions at 18° are primarily based on those of Kohlrausch.² The small modifications are due to the use of 0.496, instead of 0.497, for the cation-transference number of potassium chloride and to the change to the 1911 atomic weights. The values for the univalent ions at 25° were obtained from the Λ_0 values of Table Xa, taking 0.497 as the transference number of potassium chloride, and equalizing the different values for each ion. The value

TABLE XIII.—EQUIVALENT CONDUCTANCES OF THE SEPARATE IONS.

Values at 18°.			Values at 25°.		
Cs... 68.0	Pb... 60.8	Br..... 67.7	Tl... 76.0	I..... 76.5	
Rb... 67.5	Ba... 55.4	I..... 66.6	K.... 74.8	Cl..... 75.8	
Tl... 65.9	Ca... 51.9	Cl..... 65.5	Ag... 63.4	NO ₃ 70.6	
NH ₄ .. 64.7	Sr .. 51.9	NO ₃ 61.8	Na... 51.2	BrO ₃ 54.8	
K.... 64.5	Zn... 47.0	SCN 56.7	H.... 350
Ag... 54.0	Cd... 46.4	ClO ₃ 55.1	Pb... 71.0	SO ₄ 80.0	
Na... 43.4	Mg .. 45.9	BrO ₃ 47.6	Ba... 65.2	C ₂ O ₄ 72.7	
Li ... 33.3	Cu... 45.9	F..... 46.7	Ca... 60.0
H.... 314.5	La... 61	IO ₃ 34.0	Mg... 55.0
		SO ₄ 68.5	La... 72	Fe(CN) ₆ * 110.5	
		C ₂ O ₄ 63.0			
		Fe(CN) ₆ *. 95			

¹ See for example the results of Noyes and Lombard (THIS JOURNAL, 33, 1432-3 (1911)) with two salts of exceptionally high viscosity.

² Z. Elektrochem., 13, 333 (1907).

* Ferrocyanide ion.

for the bivalent ions at both temperatures were obtained by subtracting those for the univalent ions from Λ_0 values for the uni-bivalent salts given in Table VIIIa, and equalizing the divergencies. These new values of the ionic conductances are due in large measure to Dr. W. C. Bray, for whose coöperation we are greatly indebted.

17. Change of the Equivalent Conductance with the Concentration.

A variety of functions have been proposed for expressing the change of the equivalent conductance with the concentration.¹ Of these, the exponential function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, corresponding to the ionization function $(C\gamma)^n/C(1-\gamma) = K$, may be first considered. Previous investigations have shown that the value of the exponent n varies with the nature of the salt, but usually only within the comparatively narrow limits of 1.40 to 1.60 in dilute solution, even with salts of different valence types. The function does not, however, fully express the results through the whole range of concentration from 0.0001 to 0.2 normal,² as is shown by the fact that different values of n are derived for different concentration intervals.³

This function has, however, been previously tested only with conductance or ionization values uncorrected for viscosity. Table XIV gives the values of the exponent n obtained from the corrected ionization values at 18° of Table XI, for the two concentration intervals 0.1–20 and 10–200 millinormal, by the graphical method describing in the paragraphs preceding Table VIII.

TABLE XIV.—VALUES OF n IN THE FUNCTION $C(1-\gamma) = K(C\gamma)^n$.

Milli-equiv. per liter.			Milli-equiv. per liter.			Milli-equiv. per liter.		
Salt.	0.1–20.	10–200.	Salt.	0.1–20.	10–200.	Salt.	0.1–20.	10–200.
LiCl.....	1.48	1.33	MgCl ₂	1.48	1.20	MgSO ₄	1.60	1.18
NaCl.....	1.50	1.33	CaCl ₂	1.45	1.20	ZnSO ₄	1.60	1.25
KCl.....	1.48	1.33	BaCl ₂	1.47	1.20	CuSO ₄	1.62	1.20
KBr.....	1.45	1.33	Mg(NO ₃) ₂ ...	1.47	1.20	CdSO ₄	1.62	1.20
KI.....	1.45	1.37	Ca(NO ₃) ₂ ...	1.50	1.33			
LiNO ₃	1.48	1.37	Sr(NO ₃) ₂	1.52	1.44			
NaNO ₃	1.50	1.40	Ba NO ₃) ₂ ...	1.55	1.54			
KNO ₃	1.53	1.55	Pb(NO ₃) ₂ ...	1.58	1.58			
AgNO ₃	1.53	1.55	Li ₂ SO ₄	1.52	1.33			
KClO ₃	1.50	1.45	Na ₂ SO ₄		1.33			
LiIO ₃	1.52	1.40	K ₂ SO ₄	1.50	1.33			
NaIO ₃	1.50	1.40	Tl ₂ SO ₄	1.58	1.40			
KIO ₃	1.50	1.40	K ₂ C ₂ O ₄	1.50	1.22			

It will be seen from the table that the two values of n for the two con-

¹ For reference to some of the many articles on this subject see Noyes, *Carnegie Inst. Publ.*, 63, 48 (1907).

² Cf. Johnston, *THIS JOURNAL*, 31, 1010–11 (1909).

³ Abbott and Bray, *THIS JOURNAL*, 31, 746 (1909). Bray and MacKay, *Ibid.*, 32, 920 (1910). Hunt, *Ibid.*, 33, 800 (1911).

centration intervals as a rule differ considerably, showing that the function $(C\Lambda)^n = KC(\Lambda_0 - \Lambda)$ or its equivalent $(C\gamma)^n = KC(1 - \gamma)$ with a single value of the exponent does not express the change of conductance satisfactorily through the range of concentration from 0.0001 to 0.2 normal.

It is especially noteworthy, however, that for the lower concentration interval the values become nearly identical and equal to about 1.50 for all the salts of both these types (the limits being 1.45 and 1.58). This shows that, at fairly small concentrations, at any rate, the functional relation between ionization and concentration is independent of the number of ions into which the salt dissociates—a result that is in complete disagreement with the requirements of the mass-action law.

The values of n for the higher concentration interval, on the other hand, vary greatly with different salts; thus, between 1.33 and 1.55 for the uni-univalent salts, and between 1.20 and 1.58 for the uni-bivalent salts; but again there is no systematic difference between the values for the two types of salt.

With reference to the specific substances, it may be pointed out that there is a progressive increase in the value of n with increasing atomic weight in the case of the nitrates, just as there is a progressive decrease in their ionization values; but this is not true in the case of the chlorides and sulfates. The four bi-bivalent sulfates have almost identical ionization relations. The difference in the n values for the two concentration intervals is larger than for any of the other substances.

It seemed also desirable to test with the values corrected for viscosity the simple function $\Lambda\eta/\eta_0 = B - KC^{\frac{1}{3}}$, corresponding to the expression $\Lambda = B - KC^{\frac{1}{3}}$, which Kohlrausch found to hold closely for many uni-univalent salts between the concentrations 0.001 and 0.1 normal. The experimental values of $\Lambda\eta/\eta_0$ given in Tables VIIIa and VIIIb were plotted against the corresponding values of $C^{\frac{1}{3}}$; the straight line best representing the points between 1 and 100 millinormal was drawn; and the deviations of the separate points from the line were read off. The corresponding differences (multiplied by ten) between the observed and calculated values of $\Lambda\eta/\eta_0$ are given in Table XV, together with the constants B and K of the cube-root equation corresponding to the calculated values.

An examination of Table XV shows that the deviations of the values $\Lambda\eta/\eta_0$ from those required by the cube-root equation do not exceed 0.4 unit in the case of the uni-univalent salts between the concentrations of 1 and 200 millinormal (except in the single instance of 200 millinormal KCl); but that in the case of the uni-bivalent salts deviations as large as 0.9 to 1.2 units are common even between 1 and 100 millinormal, and frequently amount to 2.5 to 4.0 units at 200 millinormal. Cadmium chloride

TABLE XV.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Delta\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\Delta\eta/\eta_0 = B - KC^{\frac{1}{2}}$.

Salt.	K.	B.	0.	0.5.	1.	2.	5.	10.	20.	50.	100.	200.	500.
KCl.....	4.275	131.5	-15	-1	+1	+1	+1	+1	± 0	-1	-3	+10	+34
NaCl.....	3.556	109.6	-7	+3	+4	+4	+3	+1	-2	-4	-3	+2	+28
LiCl.....	3.300	99.2	-4	+4	+4	+4	+2	± 0	-2	-3	-3	+3	+47
KBr.....	4.172	133.1	-9	+3	+4	+4	+3	+2	-1	-3	-2	+4	+13
KI.....	4.224	132.4	-13	± 0	+2	+1	+1	± 0	± 0	-1	+1	...	+25
KNO ₃	5.386	129.3	-30	-7	-3	± 0	+3	+4	+3	± 0	-2	-3	+4
NaNO ₃	4.138	106.9	-17	-1	± 0	+1	+1	+1	± 0	-1	-2	+2	+15
LiNO ₃	3.369	95.8	-7	+3	+3	+2	+3	+1	-1	-3	-3	+3	+16
AgNO ₃	5.164	118.6	-28	-6	-3	± 0	+2	+3	+5	-1	-3	...	+15
KClO ₃	4.942	122.0	-24	-4	-2	± 0	+3	+2	+2	-2	-2	+2	+13
KBrO ₃ ¹	4.634	114.6	-25	-1	-1	+2	+1	± 0	-2	-1	+3
KIO ₃	4.121	100.1	-16	-1	± 0	+1	+1	+2	± 0	-2	-3	+3
NaIO ₃	3.505	78.4	-10	+2	+3	+3	+3	+2	± 0	-3	-1	+3
LiIO ₃	3.181	68.1	-8	+3	+4	+4	+3	+2	-3	-3	-2	+3	+30
MgCl ₂	5.711	111.1	+3	+11	+10	+7	+1	-4	-8	-6	+6	+34	+97
CaCl ₂	6.156	117.3	+1	-1	+9	+6	± 0	-4	-9	-5	+9	+40	+121
BaCl ₂	6.430	120.8	+1	+13	+12	-1	-6	-6	+8	+38	+115
CdCl ₂	13.20	114.4	+5	+60	+49	+11	-8	-13	-3	+6	+78
Mg(NO ₃) ₂	5.660	107.4	+3	+9	+5	± 0	-4	-8	-5	+7	+34
Ca(NO ₃) ₂	6.857	114.0	-3	+13	+14	+11	+8	+4	-1	+1	+9	+33	+96
Sr(NO ₃) ₂	7.284	114.9	-12	+7	+7	+7	+3	-2	-4	-5	+6	+29	+87
Ba(NO ₃) ₂	8.635	119.5	-23	+4	-2	+9	+6	+1	-2	-5	+2	+24	+81
Pb(NO ₃) ₂	9.918	124.8	-22	+12	+12	+12	+9	+2	-7	-15	-9	+17	+95
Cd(NO ₃) ₂	6.618	110.0	-18	+44	+37	+5	-15	-3	+1	-2	+27	+104
K ₂ SO ₄	8.38	134.0	-10	+12	+9	+12	+7	+1	-5	-6	+9	+35	+147
Na ₂ SO ₄	7.199	111.8	+1	+6	+5	+8	+4	-4	-7	+4	+33
Li ₂ SO ₄	6.070	99.2	+26	+33	+32	+8	-1	-11	-10	+7	+67
Tl ₂ SO ₄	11.90	138.6	-42	+7	+6	+2	-5	-14	-15	+6	+64
K ₂ C ₂ O ₄	7.216	128.9	-14	+6	+7	+7	+2	-4	-10	-9	+6	+40

¹ Conductance values not corrected for viscosity.

TABLE XVI.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Delta\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\text{Log } \Delta\eta/\eta_0 = \text{Log } B' - K'C^{\frac{1}{2}}$.

Salt.	$10^4 K'$	B'	0.	0.5.	1.	2.	5.	10.	20.	50.	100.	200.	500.
KCl.....	15.39	132.0	-20	-30	-1	0	+1	+1	0	-2	-2	+2	+17
NaCl.....	15.97	110.3	-14	-1	0	+2	+1	+1	-1	-3	-2	+1	+18
LiCl.....	16.54	100.0	-12	0	0	+1	0	0	-2	-2	-2	+2	+18
KBr.....	15.25	133.8	-16	-1	+1	+2	+3	+2	0	-2	-2	+1	0
KI.....	15.22	132.9	-18	-2	0	0	+1	+1	+1	-1	0	+8
KNO ₃	22.23	131.8	-55	-23	-16	-11	-4	0	+3	+3	+1	-2	-9
NaNO ₃	19.29	107.8	-26	-6	-3	-1	+1	+2	+2	+1	-2	-2	-2
LiNO ₃	17.89	96.7	-16	-2	-1	0	+1	+1	+1	0	0	+4	-15
AgNO ₃	23.31	121.0	-52	-21	-16	-10	-4	0	+5	+2	0	+1
KClO ₃	20.04	122.8	-32	-7	-4	-1	+3	+4	+5	0	-2	-5	-10
KBrO ₃ ¹	20.40	115.7	-36	-6	-4	+1	+1	+1	-1	-1	-1
KIO ₃	20.69	100.9	-24	-5	-2	0	+2	+3	+2	0	-2	-1
NaIO ₃	23.29	79.7	-23	-5	-3	-1	0	0	0	-2	-1	0
LiIO ₃	25.34	69.6	-23	-5	-3	-2	0	0	0	0	-5	+3	+21
MgCl ₂	26.33	112.5	-11	+5	+6	+4	0	-3	-6	-4	+3	+22	+70
CaCl ₂	26.30	118.3	-9	+5	+6	+5	+1	-2	-7	-5	+4	+23	+73
BaCl ₂	27.00	122.0	-11	+9	+10	+1	-4	-5	+4	+22	+68
CdCl ₂	81.39	125.9	-140	-2	+3	-15	-21	-16	-6	-21	-1	+39
Mg(NO ₃) ₂	25.48	107.7	0	+11	+8	+3	-1	-6	-7	-2	+13
Ca(NO ₃) ₂	31.36	116.3	-26	0	+3	+3	+3	0	-3	-4	-1	+9	+36
Sr(NO ₃) ₂	32.66	116.4	-27	+1	+3	+5	+3	0	-2	-6	-4	+2	+17
Ba(NO ₃) ₂	40.44	123.1	-59	-10	-5	0	+3	+3	+3	-2	-3	0	+3
Pb(NO ₃) ₂	47.78	130.4	-78	-14	-7	-1	+6	+7	+4	-2	-4	0	+11
K ₂ SO ₄	33.65	136.9	-39	-2	+2	+4	+5	+1	-2	-4	+5	+24	+85
Na ₂ SO ₄	34.64	114.2	-23	-5	-4	+2	+2	-3	-6	-1	+13
Li ₂ SO ₄	38.35	105.2	-34	-4	0	-1	-2	-3	+2	+16	+55
Tl ₂ SO ₄	50.25	143.6	-92	-5	+1	+7	+6	0	-5	+1	+24
K ₂ C ₂ O ₄	29.45	130.8	-33	-2	+1	+4	+3	0	-5	-5	+5	+26

¹ Conductance values not corrected for viscosity.

and nitrate show especially large deviations. It will also be observed that the values of the constant B for the uni-univalent salts are considerably greater, as shown by the deviations at zero concentration, than the values of Λ derived with the aid of the function $\Lambda_0 - \Lambda = K(C\Lambda)^n$. This is a consequence of the fact that the cube-root function does not satisfactorily express the observed results at the very small concentrations 0.1–1.0 millinormal.

In order to find a more satisfactory expression for the results with the uni-bivalent salts, the function $\log \Lambda\eta/\eta_0 = \log B' - K'C^{\frac{1}{3}}$ was tried. Table XVI shows the deviations, computed as in the previous case, between the observed and calculated values of $\Lambda\eta/\eta_0$. A comparison of these deviations with those of Table XV shows there is not much choice between the two functions in the case of the uni-univalent salts, but that the logarithmic one is as a rule considerably better for the uni-bivalent salts. Thus the deviations from this function between 1 and 100 millinormal seldom exceed 0.7 unit (except in the case of cadmium chloride).

The function $\Lambda\eta/\eta_0 = B'' - K''C^n$ (where n is a smaller power of the concentration than $\frac{1}{3}$) was also tried with a few of the uni-bivalent salts. The deviations are given in Table XVII:

TABLE XVII.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Lambda\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\Lambda\eta/\eta_0 = B'' - K''C^n$.

Salt.	n .	B'' .	0.	1.	2.	5.	10.	20.	50.	100.	200.
CaCl ₂	0.15	136.8	—194	0	+4	+2	+6	+2	—3	—3	0
Pb(NO ₃) ₂	0.25	134.4	—118	—7	—1	+5	+2	+6	—9	—9	0
Mg(NO ₃) ₂	0.20	116.2	—85	—1	+3	+4	+3	—1	—3	—1	+8
K ₂ SO ₄	0.20	148.2	—152	—7	0	+5	+4	0	—6	—5	+5
Na ₂ SO ₄	0.20	123.4	—115	—8	+1	+5	+3	...	—5	—6	0

These results show that for all these uni-bivalent salts a close agreement with the observed values can be secured between the concentrations 2 and 200 millinormal by employing the exponent 0.20 (instead of 0.33).

It will be seen that none of these empirical functions, even though they contain three arbitrary constants, expresses the conductance through the whole range of concentration from 0.1 to 200 millinormal. Thus, if any of the functions is made to apply through the higher concentration interval, it shows considerable deviations at the lower concentrations, and *vice versa*.

By employing a function with four empirical constants a closer agreement with the observed values over a wider range can, of course, be obtained. Reference will be made here to only one such function—that recently employed by C. A. Kraus. This function has the form $\frac{(C\Lambda)^2}{C(\Lambda_0 - \Lambda)} = K' + D'(C\Lambda)^m$ corresponding to $\frac{(C\gamma)^2}{C(1 - \gamma)} = K + D(C\gamma)^m$. As will be

shown in a contribution from this laboratory soon to be published by C. A. Kraus and W. C. Bray, this function has, in the case of uni-univalent salts, an extraordinary range of applicability. Thus it expresses satisfactorily the results from very small concentrations up to fairly high concentrations (0.5 normal and beyond) not only for solutions in water, but in a variety of non-aqueous solvents. It has, moreover, an obvious theoretical interpretation in the sense that the term $D(C\gamma)^m$ expresses the fact that the mass-action expression $(C\gamma)^2/C(1-\gamma)$ increases with the ion concentration $C\gamma$ in the solution. The function requires, moreover, that when $C\gamma$ becomes sufficiently small, the mass-action law hold true for any solute in any solvent. In the case of aqueous solutions of salts, strong acids, and bases, the value of K is so small in comparison with $D(C\gamma)^m$, except at small concentrations, that as has been seen above, an equation which contains only the latter term expresses the actual conductance fairly well within a limited concentration interval. This function appears to furnish by far the most general and satisfactory expression thus far discovered of the relation between the conductance and concentration of the uni-univalent salts. Further discussion of it in this article is, however, inappropriate, as it will be fully treated in the future paper just referred to.

In the case of salts of the uni-bivalent and higher types, the relation between concentration and ionization is probably further complicated by the presence of the intermediate ion. The most probable assumptions which can be employed for estimating its concentration in solutions of uni-bivalent salts have been discussed by W. D. Harkins in a recent contribution from this laboratory.¹

BOSTON, FEBRUARY, 1912.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 81.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. IV. COMPARISON OF THE IONIZATION VALUES DERIVED FROM THE FREEZING POINT LOWERING AND FROM THE CONDUCTANCE RATIO.

BY A. A. NOYES AND K. G. FALK.

Received February 17, 1912.

CONTENTS.—18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio. 19. Discussion of the Ionization Values Derived by the Two Methods.

18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio:

In Table XVIII are brought together the values of the percentage ionization (100 γ) corresponding to the mol-numbers derived from the

¹ THIS JOURNAL, 33, 1863 (1911).

freezing point and presented in Table II, Part I,¹ and those corresponding to the conductance-viscosity ratio at 18° presented in Table XI, Part III,² of this series. It has already been shown in Section 15 of Part III that the conductance ratio for salts at 18° does not differ from that at 0° by more than the experimental errors commonly involved in the 0° values, so that an appreciable error is not introduced in employing the 18° values for the comparison.

The ionization values derived from the freezing point are preceded by the letters FP, those from the conductance-viscosity ratio by the letters CR. The figures at the head of the table express the concentration in milli-equivalents per liter.

TABLE XVIII.—IONIZATION VALUES DERIVED FROM FREEZING POINT LOWERING AND FROM THE CONDUCTANCE-VISCOSITY RATIO.

Substance.	Method.	5.	10.	20.	50.	100.	200.	500.
KCl	FP.....	96.3	94.3	91.8	88.5	86.1	83.3	80.0
"	CR.....	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NH ₄ Cl	FP.....	94.7	92.8	90.7	87.8	85.6	83.2
"	CR.....	94.1	92.1
NaCl..	FP.....	95.3	93.8	92.2	89.2	87.5	85.0	82.4
"	CR.....	95.3	93.6	91.6	88.2	85.2	81.8	77.3
CsCl	FP.....	93.0	89.2	86.3	82.9	77.8
"	CR.....	95.4	93.7	84.7
LiCl	FP.....	94.4	93.7	92.8	91.2	90.1
"	CR.....	94.9	93.2	89.0	87.8	84.6	81.2	76.6
KBr	FP.....	92.9	88.9	86.3	83.9	81.3
"	CR.....	95.5	94.0	92.1	88.8	85.9	82.5	76.6
NaNO ₃	FP.....	90.3	88.5	85.5	83.0	79.8	...
"	CR.....	95.0	93.2	91.0	87.1	83.2	78.8	71.9
KNO ₃	FP.....	90.1	88.0	83.6	78.1	71.1
"	CR.....	95.3	93.5	91.1	86.7	82.4	77.2	68.8
KClO ₃	FP.....	91.4	89.1	84.9	79.8
"	CR.....	95.2	93.3	91.0	86.6	82.7	78.0	70.3
KBrO ₃	FP.....	92.3	89.6	85.4	80.5
"	CR.....	95.4	93.4	91.0	86.8
KIO ₃	FP.....	94.1	91.3	88.2	82.8	76.5
"	CR.....	94.6	92.8	90.3	86.0	81.9	77.5
NaIO ₃	FP.....	93.9	91.6	89.0	84.2	77.3
"	CR.....	93.9	91.7	89.0	84.2	80.1	75.2
KMnO ₄	FP.....	93.8	92.1	91.3
"	CR.....	96.8	95.1	93.0
HCl	FP.....	99.1	97.5	95.7	93.3	91.7
"	CR.....	98.1	97.2	96.2	94.4
HNO ₃	FP.....	97.4	96.0	94.2	91.2	90.0	87.9
"	CR.....	97.0	94.0

¹ THIS JOURNAL, 32, 1026 (1910).

² See the preceding article.

TABLE XVIII (continued).

Substance.	Method.	5.	10.	20.	50.	100.	200.	500.
BaCl ₂	FP.....	89.9	87.8	85.5	81.9	78.8	75.8
"	CR.....	88.3	85.0	79.8	75.9	72.0	67.2
CaCl ₂	FP.....	87.6	83.7	81.5	80.4
"	CR.....	91.0	88.2	84.9	80.2	76.4	72.7	68.8
MgCl ₂	FP.....	88.5	85.4	83.9	83.3
"	CR.....	91.0	88.3	85.1	80.3	76.5	72.8	68.7
CdCl ₂	FP.....	79.1	76.8	69.0	60.5	53.9
"	CR.....	80.3	73.5	66.4	55.9	45.3	37.5	28.9
CdBr ₂	FP.....	78.0	70.4	58.9	48.2	36.7
"	CR.....	74.9	66.1	57.3
CdI ₂	FP.....	59.3	54.0	40.0	22.5	10.0
"	CR.....	67.5	57.3	46.9
Cd(NO ₃) ₂	FP.....	94.8	92.1	90.1	88.7	88.4
"	CR.....	91.7	87.1	84.8	79.2	73.1	68.4	62.8
Ba(NO ₃) ₂	FP.....	91.7	88.8	85.5
"	CR.....	89.8	86.1	81.8	74.4	67.9	60.9	50.4
Pb(NO ₃) ₂	FP.....	89.0	85.0	80.4	72.4	64.9	56.8	42.7
"	CR.....	88.6	84.5	79.3	70.8	63.5	55.9	45.4
K ₂ SO ₄	FP.....	92.9	89.9	85.7	78.5	73.0	66.7	56.8
"	CR.....	90.5	87.2	83.2	77.1	72.2	67.3	61.8
Na ₂ SO ₄	FP.....	86.7	79.5	73.6	67.2	56.7
"	CR.....	89.3	85.7	75.6	70.4	65.2
MgSO ₄	FP.....	69.4	61.8	53.6	42.0	32.4	22.3	8.4
"	CR.....	74.0	66.9	59.6	50.6	44.9	40.3
CuSO ₄	FP.....	61.6	54.5	45.5	31.8
"	CR.....	70.9	62.9	55.0	45.5	39.6	35.1
ZnSO ₄	FP.....	66.5	58.2	48.9
"	CR.....	71.0	63.3	55.6	46.4	40.5	36.0
CdSO ₄	FP.....	65.8	56.9	47.7	34.3
"	CR.....	69.4	61.4	53.4	43.7	37.7	33.2	29.0
K ₃ Fe(CN) ₆	FP.....	89.4	86.8	77.8
"	CR.....	86.9	82.7
K ₄ Fe(CN) ₆	FP.....	63.4	58.1	52.0	42.5
"	CR.....	59.1	53.8	49.8

19. Discussion of the Ionization Values Derived by the Two Methods.

A comparison of the two sets of ionization values at the concentrations between 20 and 100 millinormal inclusive shows the following deviations:

KCl, NH₄Cl, and KBr: less than 1% of the ionization value.

NaCl and CsCl: 1 to 2%.

LiCl: 4 to 6%.

NaNO₃ and KNO₃: 3 to 5%; but the probable accuracy of the freezing-point results is in these cases small.

KClO₃ and KBrO₃: 2 to 4%.

KIO₃: 2 to 7%, increasing with the concentration.

NaIO₃: practically zero up to 50, 3.5% at 100 millinormal.

HCl: 0.3 to 1.2%; yet the values are 5 to 10% greater than those for neutral salts.

BaCl₂: 1 to 4%, increasing with the concentration.

CaCl₂ and MgCl₂: 3 to 9%, increasing with the concentration.

CdCl₂, CdBr₂, CdI₂, and Cd(NO₃)₂: much larger deviations than with the other uni-bivalent salts.

Pb(NO₃)₂ and K₂SO₄: not more than 2%, even up to 200 millinormal.

Na₂SO₄: about 5%.

MgSO₄, CuSO₄, ZnSO₄, CdSO₄: very large deviations.

K₄Fe(CN)₆: 7 to 8%.

It will be seen from this summary that the two methods give ionization values which for most uni-univalent substances agree with each other within 2% up to 0.1 normal; and that the same is true of the uni-bivalent salts, potassium sulfate and lead nitrate, even up to 0.2 normal. The halides and sulfates of bivalent metals (and also lithium chloride and sodium sulfate) on the other hand show, as a rule, much larger deviations than this at 0.1 and 0.2 normal.

In considering the significance of the comparison of the ionization values, the principles involved in their derivation should be recalled. The calculation of ionization from freezing-point lowering is based on the principle that the molal effects of the ions and of the unionized substance are normal, like those of organic substances. The calculation of ionization from the conductance-viscosity ratio is based on the principle that the equivalent conductance or mobility of the ions does not vary with the concentration, except in so far as the fluidity of the solution varies. Both methods involve also the assumption that the only forms in which the substance exists in the solution are the unionized molecules and the ultimate simple ions into which they dissociate at extreme dilution.

As this last assumption is probably fulfilled in the case of most uni-univalent substances, the agreement of the two sets of ionization values for these substances might seem to substantiate the principles involved in the two methods. There is, however, the possibility that the agreement arises from a corresponding inaccuracy in both of the principles, or from a compensation of errors in the case of the freezing-point values arising from the unionized molecules having an abnormally large, and the ions an abnormally small, molal effect, or *vice versa*. That the agreement in reality arises from such a compensation is evident from the fact that the ionization values derived from the conductance ratio decrease with the concentration far more slowly than the mass-action law requires, showing, if these values are correct, that increase in concentration must cause an abnormally small increase in the activity of the ions or an abnormally large increase in the activity of the unionized molecules, or both. This conclusion is confirmed by other independent phenomena, especially the solubility effects,¹ which show that the activity of ions

¹ Cf. Bray, THIS JOURNAL, 33, 1684 (1911).

is somewhat decreased, and that of unionized molecules is very greatly increased, when the salt concentration or ion concentration in the solution is increased.

In the case of uni-bivalent salts the presence of the intermediate ion may introduce a further complication. It will be seen from equation (33) of Section 11 of the preceding paper that for the case that the conductance arises in part from the intermediate ion the mol-number i (which is then equal to $1 + 2\gamma_2 + \gamma_1$) must be somewhat larger (namely, by the amount $\gamma_1 \frac{\Lambda_{A-} - \Lambda_{BA-}}{\Lambda_{B+} + \Lambda_{A-}}$) than it is for the case that the conductance arises wholly from the simple ions (in which case $i = 1 + 2\gamma$). So long, however, as the proportion (γ_1) of the intermediate ion is not very large, the effect on the mol-number is not likely to be great,¹ and there may be a fairly close agreement between the two sets of ionization values, such as was observed with potassium sulfate and lead nitrate.

The effect of the formation of double molecules, such as $Mg_2(SO_4)_2$, and of complex ions, such as $Mg(SO_4)_2^-$, $BaCl_4^-$, or $BaCl_2^-$, on the other hand, can be shown (by formulating the appropriate expressions corresponding to equation (33) and the expressions for the mol-number) to decrease the mol-number and the ionization value derived from the freezing point. As was suggested by Arrhenius,² this may explain the much larger ionization values obtained from the conductance ratio in the case of the bivalent metal sulfates.

The most striking discordance between the two sets of ionization values is that presented by the bivalent metal halides, for which the values derived from the freezing point are always much larger than those derived from the conductance ratio. It has already been shown in Part II³ of this series that the transference numbers of these substances are also abnormal, namely, in the respect that the cation transference decreases markedly with increasing concentration. There appears, however, to be no chemical explanation which would account for both of these anomalies; and it seems therefore probable that physical deviations must enter as a complicating factor.

Boston, February, 1912.

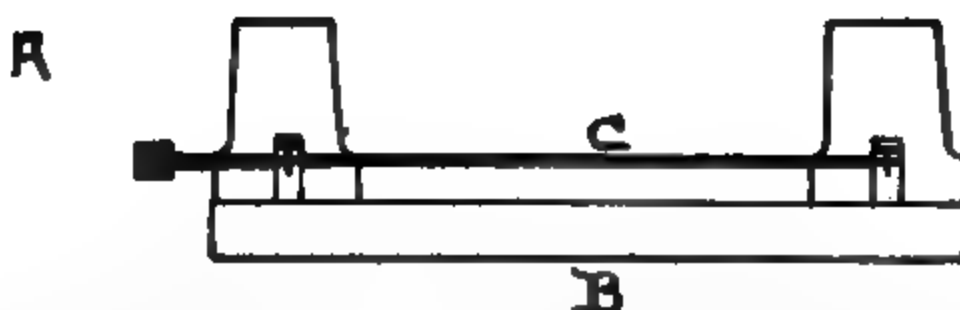
¹ Thus the calculations of Bray cited by Harkins (THIS JOURNAL, 33, 1864 (1911)) show that the conductance of a 0.1 N K_2SO_4 solution could be accounted for either by assuming 72% SO_4^{--} and 28% K_2SO_4 , or by assuming 60% SO_4^{--} , 35% KSO_4^- , and 5% K_2SO_4 . Under the former assumption, the mol-number i would be 2.44, and under the latter 2.55.

² Z. physik. Chem., 1, 639 (1887).

³ THIS JOURNAL, 33, 1454-9 (1911).

NOTES.

A Simple Method of Illustrating the Relative Conductance of Salts and Acids in Dilute Solutions.—The apparatus shown in the cut has been found useful in connection with the presentation of the ionic theory to first year students in chemistry. The relative conductance of salts in dilute solutions, the word "salts" being used in a general sense, can be readily shown on the lecture table before small classes or in the laboratory



by the students themselves. It affords a simple method of illustrating the relative strengths of acids and of bases, the effect of introducing sodium acetate into solutions acidified with stronger acids, and so on.

A is an ordinary conductivity cell with electrodes of movable platinum disks and on the outside of which is etched a millimeter scale from 0–50.

B is a small block $25 \times 6 \times 1$ cm. on which is fastened two lamp sockets connected by the wires *C*. In one of the sockets is inserted an eight candle and in the other a sixteen candle lamp. The lamps are connected with an ordinary 110 volt lighting system (alternating current) and the solutions, made up to 0.01 *N*, introduced in the cell. One electrode is fixed at the zero mark and the other raised nearly to the top of the cell. The cell is now brought into the circuit and the upper electrode carefully lowered until the filament of the smaller lamp is faintly but distinctly luminous. By throwing a cloth over the larger lamp and partially surrounding the smaller one with a sheet of black paper fairly sharp readings can be obtained. If necessary the cell can be placed in a larger vessel of water to avoid change in temperature. For less dilute solutions a larger number of lamps must be used.

The distances between the electrodes for a series of solutions will repre-

sent the relative conductivities. This might also appear to represent relative ionizations, but this is not the case. Since the mobilities of the ions differ very considerably (318 for H^+ , 43.6 for Na^+ , 35.0 for $C_2H_3O_2^-$) the relative ionizations are not proportional to the relative conductivities of the solutions.

The following are some of the results obtained:

0.01 <i>N</i> concentration.	Dist. between electrodes.		
Hydrochloric acid.....	45.5	45.5	46.5
Nitric acid.....	44.5	44.5	45.0
Sulfuric acid.....	39.0	38.5	38.5
Oxalic acid.....	19.8	18.5	19.3
Acetic acid.....	2.5	2.5	2.5
Sodium hydroxide.....	26.7	26.5	26.3
Potassium hydroxide.....	27.5	28.0	28.0
Barium hydroxide.....	27.0	27.5	27.5
Ammonium hydroxide.....	2.5	2.0	2.5
Potassium nitrate.....	15.5	16.0	15.5
Ammonium chloride.....	16.5	16.5	16.0
Sodium acetate.....	10.5	10.5	10.0

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*The Occurrence of Argon in Commercial Oxygen Made from Liquid Air.*¹—During the course of some calorimetric work it was noted that much more nitric acid was formed using an electrolytic oxygen containing 99.6% oxygen, than with an oxygen 96.9% pure, furnished by the Linde Air Products Company. After proving that neither product contained any other impurity which could account for the observed results, the Linde oxygen was tested for argon. A large sample was first treated with metallic copper to remove oxygen. The residue, consisting of argon and nitrogen, was treated with a mixture of magnesium powder and calcium oxide, according to the method of Maquenne.² The residue from this treatment, after sparking with oxygen to remove hydrogen formed during the reaction,³ and removing the excess of oxygen with pyrogallol, was pure argon. Nitrogen was determined by difference. The composition of the Linde oxygen was thus found to be 96.9% oxygen, 2.8% argon, and 0.3% nitrogen. This confirms the work of Claude,⁴ who has noted that argon to the extent of about 3% is the chief impurity in oxygen prepared by the Claude process, which he explains by the fact that the volatility of argon more closely resembles that of oxygen than that of nitrogen.

GEO. W. MORREY.

¹ Published by permission of the Director of the Bureau of Standards.

² Maquenne, *Compt. rend.*, 121, 1147-8 (1895).

³ Travers, "Experimental Study of Gases," p. 103.

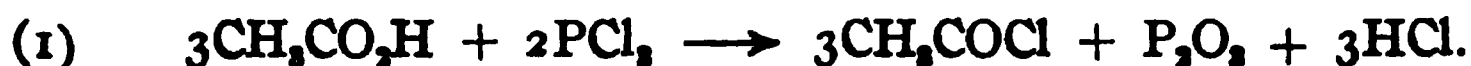
⁴ *Compt. rend.*, 151, 792-3 (1909).

THE ACTION OF PHOSPHORUS TRICHLORIDE ON ORGANIC ACIDS; MONOACETYL PHOSPHOROUS ACID.

BY BENJAMIN T. BROOKS.

Received January 22, 1912.

It is a striking fact that the course of one of the most important type reactions in organic chemistry is not definitely known. Two different reactions for the action of phosphorus trichloride on organic acids are given in the latest editions of standard text books of organic chemistry. Thus, for the preparation of acetyl chloride Beilstein,¹ Meyer and Jacobson² and Gatterman³ give the equation



Richter⁴ and Holleman⁵ give the equation



As indicated above, one equation represents the formation of the acid chloride and *phosphorous acid* while the other gives the acid chloride, *phosphorous oxide* and hydrochloric acid as the products of the reaction.⁶ As a matter of fact, the evolution of hydrochloric acid in considerable quantities is always observed in carrying out this reaction and to explain this fact it has been assumed that the phosphorous acid, which is first formed, reacts with a second molecule of the trichloride to give free HCl and P_4O_6 , which result is expressed in equation (1). This latter assumption is directly contradictory to the results of Thorpe and Tutton,⁷ who showed that in the first place hydrogen chloride reacts very readily with P_2O_3 or P_4O_6 , according to the following equation:



They also showed that phosphorous acid and phosphorus trichloride react together only *very slowly* and probably in accordance with the following equation, confirming the work of Geuther⁸ on this subject:

¹ "Handbuch d. Org. Chem.," Ed. 1893, Bd. I, 458.

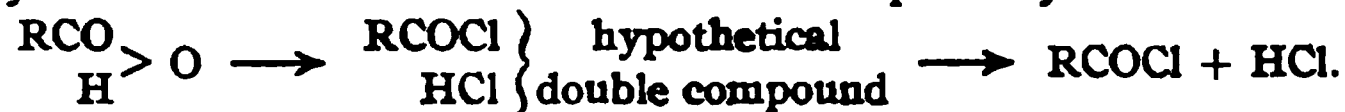
² "Lehrbuch d. Org. Chem.," 2nd Ed., 1907, Bd. I, 561.

³ "Practical Methods of Organic Chemistry." Translation of 4th German edition by W. B. Schober, 1905, p. 122.

⁴ "Organische Chemie." Eleventh Edition, Bonn, 1909. To prepare acetyl chloride the author recommends the proportions required by equation [1].

⁵ "Organic Chemistry." A. F. Holleman. Translation of 2nd Dutch edition by A. J. Walker, New York (1904), p. 114.

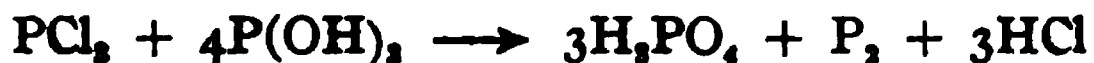
⁶ Delacre (*Chem. Zentr.*, 1902, I, 1197) agrees with equation (1) and advances the theory that the mechanism of the reaction is probably



There is no experimental evidence of the existence of such a double compound and in view of the data brought forward in the present paper such an assumption is not in accord with the facts. Tissier (*Ann. chim. phys.*, [6] 29, 384) advanced the equation $6\text{RCO}_2\text{H} + 3\text{PCl}_3 \longrightarrow 6\text{RCOCl} + [\text{H}_3\text{P}_2\text{O}_6] + 3\text{HCl}$.

⁷ *J. Chem. Soc.*, 59, 1019 (1891).

⁸ *J. prakt. Chem.*, [2] 8, 359 (1874).



Thus Thorpe and Tutton obtained 4.0 g. PCl_3 , 1.5 g. H_3PO_4 , 2.7 g. H_2PO_3 and 0.4 g. phosphorus from 5.0 g. P_4O_6 and an excess of hydrogen chloride in an experiment which lasted one week. Therefore, if this work of Thorpe and Tutton and of Geuther is correct, and there appears to be no reason to doubt it, the liberation of the large quantities of hydrochloric acid in the preparation of the chlorides of organic acids by phosphorus trichloride cannot result from the action of the chloride on phosphorous acid. However, the work of Thorpe and Tutton¹ and of Thorpe² is contradictory since in the latter publication the author considers that the yields³ point definitely to equation (1).

I have found that one source of the hydrogen chloride evolved in the reaction in question is the reaction of acetyl chloride on phosphorous acid yielding an acetyl derivative, probably a mixed acid anhydride of

the formula $\text{P} \begin{matrix} \text{OH} \\ \diagup \\ \text{OH} \\ \diagdown \\ \text{O}.\text{OC}.\text{CH}_3 \end{matrix}$. On adding pure acetyl chloride to crystallin

phosphorous acid hydrogen chloride is evolved, slowly at 20° but quite rapidly on warming to 50°. One and possibly two hydroxyl groups enter into the reaction, depending upon the duration of the reaction and the removal of the hydrochloric acid.

The well known use of acid chlorides in testing for hydroxyl groups appears not to be strictly limited to alcohols since, as is well known, the chlorides of organic acids may also react with the hydroxyl in the carboxyl group, forming anhydrides, the degree of completion of the reaction depending upon the removal of hydrogen chloride. According to Anschütz,⁴ the reaction between acetyl chloride and acetic acid is slow and incomplete, but Wedekind⁵ has stated that the addition of a tertiary amine serves to remove hydrochloric acid and good yields of anhydride may be obtained in this manner. In phosphorous acid there are two and possibly three hydroxyl groups⁶ and it is therefore to be expected that the chlorides of organic acids will react with it, giving a mixed acid anhydride. I have found that warming to the boiling point of acetyl

¹ *Loc. cit.*

² *J. Chem. Soc.*, 37, 186 (1880).

³ Thorpe does not describe the methods employed by him to determine the yields of hydrochloric acid and acetyl chloride. As ordinarily carried out, both phosphorus trichloride and acetyl chloride are carried over by the hydrochloric acid in considerable quantities, and furthermore the acetyl chloride obtained, when the amounts of the reacting substances required by equation (1) are taken, contains much phosphorus trichloride and hydrochloric acid. It is obviously impossible to arrive at quantitative data, with respect to these products, by fractional distillation.

⁴ *Ann.*, 226, 5 (1884).

⁵ *Ber.*, 34, 2070 (1901). Compare Tschitschibabin, *Chem. Zentr.*, 1901, II, 543.

⁶ Compare Vorländer, *Ann.*, 320, 114 (1902).

chloride under a return condenser removes the hydrogen chloride completely enough for the reaction to proceed smoothly.

The compound $\text{P} \begin{array}{l} \text{OH} \\ \text{OH} \\ \text{O.OCCCH}_3 \end{array}$ is analogous with the so-called mixed acid anhydrides recently prepared by Fry, Francis, and Pictet and his students. Acetic anhydride and nitric anhydride give the nitrate $\text{CH}_3\text{COONO}_2$,¹ benzoyl chloride and silver nitrate give benzoyl nitrate² and chromyl chloride and potassium acetate yield the diacetyl derivative of chromic acid.³ Acetyl compounds of boric and arsenious acids are also known, the former being easily prepared by the action of acetyl chloride on boric acid. A mixed anhydride of phosphoric and acetic acids of doubtful composition was made by Carius and Kämmerer⁴ to which they assigned the formula $\text{P}_2\text{H}_2\text{O}_5(\text{C}_2\text{H}_3\text{O})_2$ and stated that it was decomposed by water to acetic and phosphoric acids. Menschutkin⁵ attempted to prepare an acetyl derivative of phosphorous acid by heating with acetyl chloride to 120° in a bomb tube. The reaction product was *poured into water* and a lead salt prepared which contained organic matter and which the author regarded as probably $\text{P}_2\text{H}_2\text{O}_5(\text{C}_2\text{H}_3\text{O})$.

In addition to the isolation of monoacetylphosphorous acid I have proven that when acetyl chloride is prepared according to equation (1) no phosphorous oxide is formed, the residue consisting of phosphorous acid and a small amount of the acetyl derivative. The phosphorus trichloride in excess of that required by equation (2) was recovered unchanged. Furthermore the evolution of hydrochloric acid from the action of acetyl chloride on pure crystallin phosphorous acid has been determined quantitatively and although a diacetyl derivative has not been isolated the amount of hydrochloric acid given off under certain conditions seems to indicate that a diacetyl derivative may be formed.

Discussion of the Reaction.

Since chlorides of organic acids may be prepared by treating the acid with hydrogen chloride and a dehydrating agent, it is not unreasonable to assume that the reaction under discussion is catalyzed by a trace of water and that the phosphorus trichloride serves both as a source of hydrochloric acid and as a dehydrating agent. However, in view of the results of Autenrieth and Geyer⁶ on the reaction between phosphorus pentachloride and phenols it seems probable that the chlorides of phosphorus are able to react directly with hydroxyl in any compound. More-

¹ Pictet and Khotinsky, *Ber.*, 40, 1163 (1907).

² Francis, *Ibid.*, 39, 3798 (1906).

³ Fry, *THIS JOURNAL*, 33, 690 (1911).

⁴ *Ann.*, 131, 170 (1864).

⁵ *Ibid.*, 133, 317 (1865).

⁶ *Ber.*, 41, 146 (1908).

over, it is shown in the present communication that the chloride of the acetyl group, which radical possesses only a small negative polarity,¹ reacts with phosphorous acid, which is a comparatively strong acid. The known data concerning the reactivity of other acid chlorides upon hydroxyl derivatives are extremely meager, but it appears reasonable to assume that the point of equilibrium in such reactions will depend upon the relative polarity of the atoms or radicles bound to the hydroxyl group or chlorine atoms. A very similar reaction is that of benzene sulfochloride on alcohol, the velocity of which is accelerated by the substitution of chlorine, bromine or iodine in the phenyl group.² It is almost impossible to prepare trichloroacetyl chloride by the action of phosphorus trichloride on trichloroacetic acid, the yield being extremely small. The ease with which such weak acid-forming substances as AsCl_3 , SbCl_3 , SiCl_4 , AlCl_3 , FeCl_3 , and COCl_2 hydrolyze with water suggests that our knowledge of the behavior of these substances toward hydroxyl derivatives could be very greatly extended.

Experimental Part.

Action of Acetyl Chloride on Phosphorous Acid.—The liberation of hydrogen chloride by the action of acetyl chloride on pure, crystallin phosphorous acid was quantitatively measured in the following manner: The reaction mixture was warmed to 50° under a return condenser and the hydrochloric acid liberated was absorbed in water. An aliquot part of the aqueous acid solution was titrated for total acidity and then for total chlorine as chloride. The hydrochloric acid set free and acetyl chloride carried over may readily be calculated from these results. Thirty-five grams of acetyl chloride were added to 10 g. crystallin phosphorous acid. The liberation of hydrochloric acid began at room temperature and at 50° was quite rapid. At the end of two hours the aqueous solution in which the gases were absorbed was titrated and the results found may be stated as follows:

	Grams.
Hydrogen chloride liberated.....	6.734
Hydrogen chloride calculated for mono-acetyl derivative.....	4.44
Acetyl chloride carried over.....	3.214

A repetition of the above experiment, using 15.6 g. phosphorous acid and 35.0 g. acetyl chloride, gave, in $1\frac{1}{2}$ hours:

	Grams.
Hydrogen chloride liberated.....	7.677
Hydrogen chloride calculated for mono-acetyl derivative.....	6.65
Acetyl chloride carried over.....	2.115

A third experiment was made with the hope of isolating an acetyl

¹ Derick, *THIS JOURNAL*, 33, 1156 (1911).

² Goubeau, *Chem. Zentr.*, 1911, II, 18.

compound of phosphorous acid. In this experiment 75 g. acetyl chloride set free 28.61 g. of hydrochloric acid from 65 g. phosphorous acid during 4 hours on the water bath. A white crystallin crust formed on the surface of the phosphorous acid, but it was found to be impossible to isolate this substance in a pure condition.

The mono-acetyl derivative of phosphorous acid was prepared in a state of purity in the following way: Five grams of phosphorous acid were diluted in 40 cc. acetic anhydride at room temperature. To this solution 10 cc. acetyl chloride were added and the mixture warmed to 50° , at which temperature a white crystallin substance was deposited. After standing for 20 minutes at this temperature the supernatant liquid was decanted, the crystals washed five times with dry ether and the remaining ether removed at ordinary temperature by exhausting to 10 mm.

The substance was analyzed by heating with fuming nitric acid to 160° in a bomb tube. The phosphoric acid thus obtained was determined gravimetrically.

0.2403 g. substance gave 0.2210 g. $\text{Mg}_3\text{P}_2\text{O}_7$, corresponding to 25.30% phosphorus; calculated for $\text{CH}_3\text{CO}.\text{PO}_3\text{H}_2$, 25.00% P.

Attempts to prepare this substance by employing acetic anhydride alone gave brown, tarry smears which were not further investigated. It was also observed that phosphoric anhydride reacts energetically with acetic anhydride with charring and evolution of considerable heat.

Action of Phosphorus Trichloride on Acetic Acid.—In the first experiment of this series 40 g. phosphorus trichloride (1 molecule) and 52.5 g. acetic acid (3 molecules) were employed. The two substances were simply poured together and warmed on the water bath for half an hour under a return condenser, in the usual manner. The gases were absorbed in water as in the previous experiments. It was assumed that both phosphorus trichloride and acetyl chloride would be carried over in considerable quantities with the hydrogen chloride. These substances were quantitatively determined in the following manner: Phosphorus trichloride was calculated from a determination of phosphorous acid, the latter substance being determined by boiling an aliquot part of the solution with bromine water and determining the phosphoric acid thus formed. Acetyl chloride was calculated from the acetic acid formed. The acetic acid was determined from the total acidity minus the phosphorous and hydrochloric acids. (It was found to be possible to titrate phosphorous acid with sodium hydroxide against phenolphthalein within about 1.0% of the correct value, since the hydrolysis of Na_2HPO_4 in concentrated solutions is very slight.) The total chlorine was determined by titration with silver nitrate. The experiment may be summarized as follows:

Gases:	Grams.
Hydrogen chloride liberated.....	10.67
Hydrogen chloride calculated for [1] Thorpe's equation	15.91
Acetyl chloride carried over.....	7.347
Phosphorus trichloride carried over.....	0.452
Distillate:	
Weight of crude distillate (acetyl chloride and acetic anhydride)	43.0
Weight of distillate boiling from 50–55°.....	20.2
Total acetyl chloride formed approximately.....	27.5
Residue:	
Weight.....	28.4
Weight of residue calculated for P_4O_6	15.8
Weight of residue calculated for H_3PO_3	24.2
Weight of residue minus acetic acid removed by distillation with steam.....	23.6

The residues evidently consisted of phosphorous acid and a small proportion of the acetyl derivative. The residue was heated to 100°–105° and a vacuum of 14 mm. applied but nothing distilled over. It is therefore conclusively shown that no phosphorous oxide is formed under these conditions, since this substance is a liquid distilling in a vacuum of 18 mm. at 64.4°. The residue completely freed from acetyl chloride and acetic anhydride by this treatment was subjected to steam distillation and 5.07 g. acetic acid obtained. From the above facts it is probable that in the formation of the acetyl derivative present in the residue, phosphorous acid itself is first formed.

Action of Phosphorus Trichloride on Acetic Acid According to Thorpe's Equation.—In the following experiment 35 g. of phosphorus trichloride (2 mol.) were added to 22.8 g. glacial acetic acid. The experimental procedure and methods of calculation were the same as in the previous experiments, the reaction mixture being warmed on the water bath for one-half hour. The results obtained may be summarized as follows:

Gases:	Grams.
Hydrogen chloride liberated.....	3.808
Acetyl chloride carried over.....	5.250
PCl_3 carried over.....	1.203
Distillate:	
Acetyl chloride.....	23.44
PCl_3	11.15
Hydrogen chloride.....	0.94
Residue:	
Weight.....	13.1

The distillate was analyzed by pouring into water and determining the phosphorous acid, hydrochloric acid and acetic acid as described above. The large amount of phosphorus trichloride recovered is particularly worthy of note. The residue could not be distilled at 100°

and 14 mm. Analysis showed it to contain 36.02% phosphorus; calculated for H_3PO_3 , 37.80%.

These facts show conclusively that also under these conditions no phosphorous oxide is formed. Equation (1) is therefore wrong.

The low per cent of phosphorus in the residue and the hydrochloric acid liberated are probably due to the formation of a small amount of the mixed anhydride.

The Formation of Acetic Anhydride.—Thorpe suggested that the formation of acetic anhydride in his experiments might have been due to the dehydrating action of the phosphorous oxide on acetic acid or to the action of acetyl chloride on acetic acid. According to my results the latter view is the correct one.

As the preparation of acetyl chloride is ordinarily carried out the yield is considerably diminished by the formation of acetic anhydride, unless a large excess of PCl_3 is taken. It is commonly observed that if the quantities required by equation (1) are taken, little or no acetic anhydride is formed. The reason for this becomes readily apparent if one considers the equilibrium



and the effect which the addition of PCl_3 would have upon such a mixture in equilibrium. Obviously, the result would, by the removal of acetic acid with the formation of more acetyl chloride, lead to the conversion of more anhydride into chloride, *provided* that the hydrogen chloride had not been removed by the return condenser route. If this is the function of the excess of phosphorus trichloride it should be possible to obtain acetyl chloride by passing hydrochloric acid into a mixture of acetic anhydride and phosphorus trichloride. This is corroborated by the following experiment:

Dry hydrogen chloride was passed into a mixture of 25 g. acetic anhydride (3 molecules) and 15 g. phosphorus trichloride ($1\frac{1}{4}$ molecules). Hydrogen chloride was rapidly absorbed, the solution becoming warm and depositing phosphorous acid. Distillation gave 36.5 g. acetyl chloride boiling between $50\text{--}57^\circ$, the theoretical yield being 38.4 g. Doubtless a small quantity of acetylphosphorous acid was also formed.

The results of the above experiment indicated that on the preparation of acetyl chloride according to equation (2), as ordinarily done in the laboratory, *i. e.*, under a return condenser, the hydrochloric acid necessary for the conversion of the acetic anhydride into the chloride is removed from the reaction mixture. This view is supported by the following experiment: Twenty-five grams of glacial acetic acid (3 molecules) were treated with 24 g. phosphorus trichloride ($1\frac{1}{4}$ molecules) and the

reaction mixture allowed to stand at 18° for six hours under a slight pressure (equal to 10 cm. concentrated sulfuric acid). A small amount of hydrochloric acid was slowly and regularly given off. On distillation 31.0 g. acetyl chloride boiling from 50° to 55° were obtained; theoretical yield, 32.5 g. It is therefore evident that the formation of acetic anhydride can be reduced to almost nil by a simple modification of the experimental conditions. So far as reduction of the yield of chloride is concerned the formation of acetic anhydride is usually a more serious factor than the formation of acetylphosphorous acid.

In conclusion, it might be stated that the yellow or brown color of the phosphorous acid residue, which is often assumed to be due to phosphorus, is probably due to the decomposition of acetylphosphorous acid since it has been observed that at approximately 100° this substance melts with slight decomposition turning yellow to brown in color.

Summary.

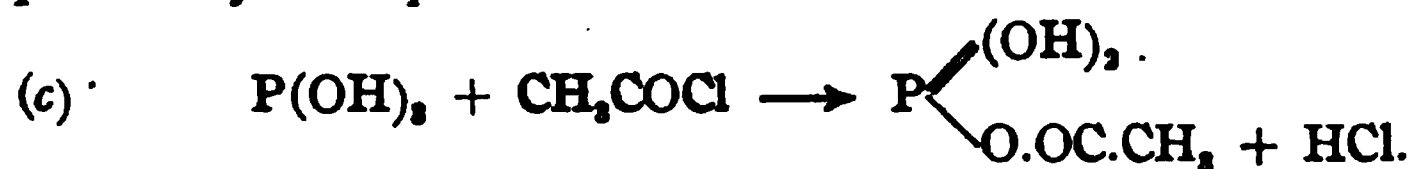
It has been proven that the action of phosphorus trichloride on acetic acid may be represented by the following equations:



Two secondary reactions take place, the most important of which is expressed by the reaction



This reaction may be minimized by a simple modification of the conditions of the experiment. The secondary reaction next in importance is the formation of a mixed anhydride of phosphorous and acetic acids expressed by the equation



The equation, given in many standard books, expressing the reaction of phosphorus trichloride on acetic acid with the formation of phosphorous oxide is unqualifiedly wrong.

It is obviously possible to extend and amplify this investigation in many directions, and the author regrets that the press of other work prevents further experiments along these lines.

The author desires to express his indebtedness to Professor William McPherson, of Ohio State University, for first calling his attention to our unsatisfactory knowledge of the reaction discussed above.

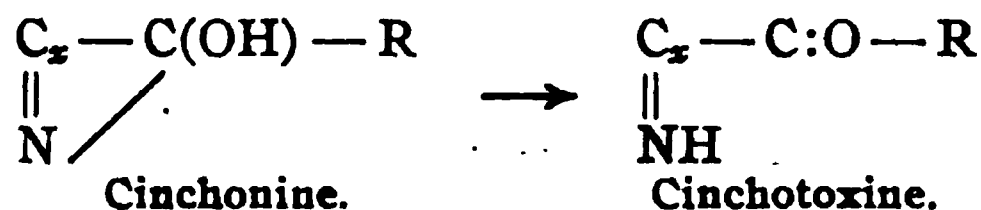
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]
**THE CONVERSION OF CINCHONINE AND QUININE INTO THEIR
 POISONOUS ISOMERS, CINCHOTOXINE AND QUINOTOXINE,
 AND THE RELATION OF THIS CONVERSION TO THE
 TOXICITY OF THE CINCHONA ALKALOIDS.¹**

By H. C. BIDDLE.²

Received February 3, 1912.

It was shown by v. Miller and Rohde,³ in 1895, that prolonged heating of cinchonine with acetic acid at a temperature of 100° leads to the formation of a substance isomeric with cinchonine, to which, because of its poisonous properties, they gave the name of cinchotoxine. From its method of preparation and its low optical activity, they suspected this new substance to be identical with a similar isomeric body, cinchonidine, which had been obtained more than forty years before by Pasteur⁴ through fusion of the salts of cinchonine, preferably the bisulfate, and which had subsequently been studied by a number of investigators.⁵ Cinchotoxine, however, was obtained by v. Miller and Rohde in a crystalline form differing from that of cinchonidine. This discrepancy remained unexplained until five years later, when Brunner⁶ showed that the substance is dimorphic in its crystalline habit and is in every way identical with the cinchonidine of Pasteur.

The chemical properties of cinchotoxine indicate that it is a secondary base containing a ketone grouping in the molecule.⁷ Cinchonine itself is a tertiary base with a hydroxyl group in the molecule. The transformation of cinchonine into cinchotoxine may, consequently, be represented by the following molecular change:



This rearrangement takes place in the so-called "second half" of the cinchonine molecule and is indicated somewhat more clearly in the following possible formulas of Rabe,⁸ which, among others, have been suggested for cinchonine and cinchotoxine:

¹ Biddle, Preliminary report before the 42nd meeting of Am. Chem. Soc., San Francisco, July, 1910 (Abstract in *Science*, 32, 486).

² The experimental work in this investigation has in part been carried out in conjunction with two of my students, O. L. Brauer and T. B. Kelly.

³ Miller and Rohde, *Ber.*, 27, 1187, 1279 (1894); 28, 1056 (1895).

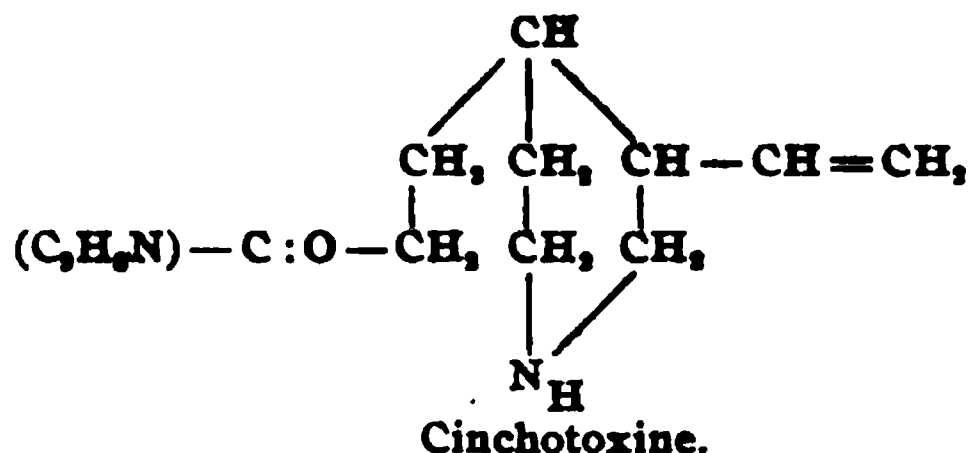
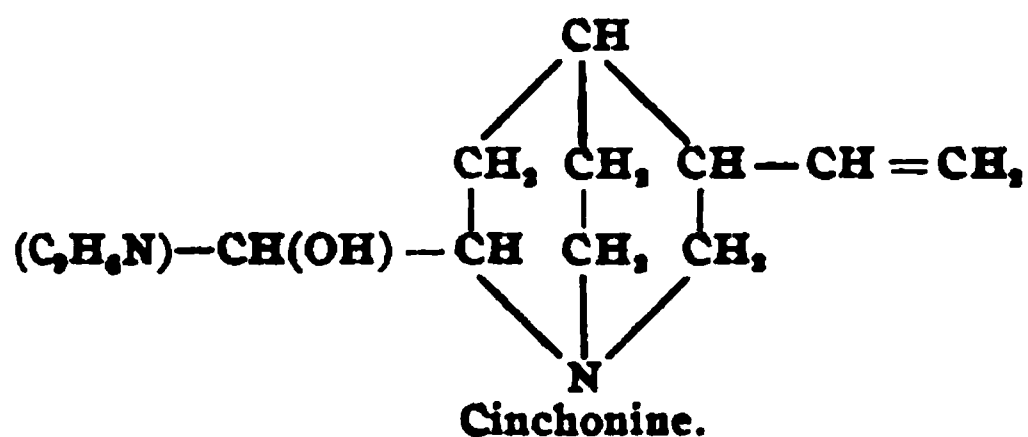
⁴ Pasteur, *Jahrb.*, 1853, 473; *Compt. rend.*, 37, 110 (1853).

⁵ Hesse, *Ann.*, 147, 242 (1868); 166, 277 (1873); 178, 253 (1875). Howard, *J. Chem. Soc.*, 25, 102 (1872). Roques, *Bull. soc. chim.*, [3] 13, 1007 (1895).

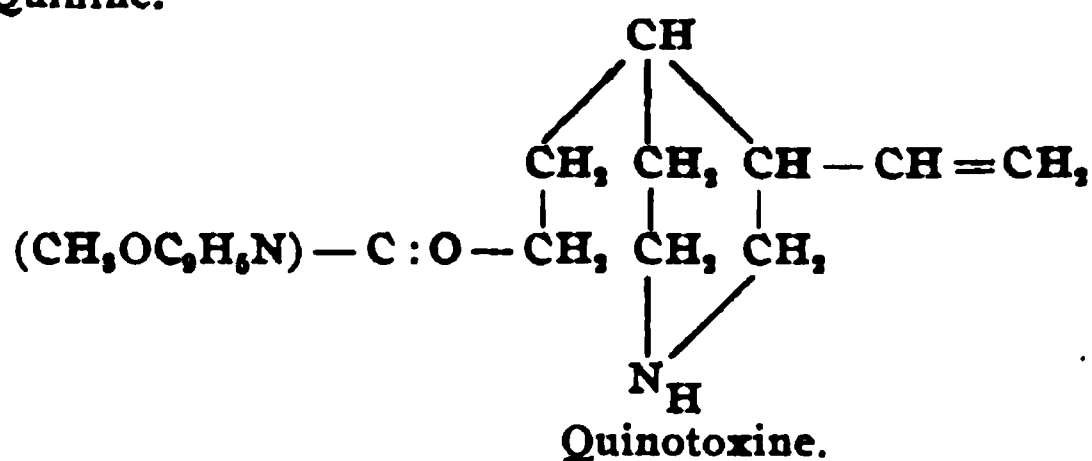
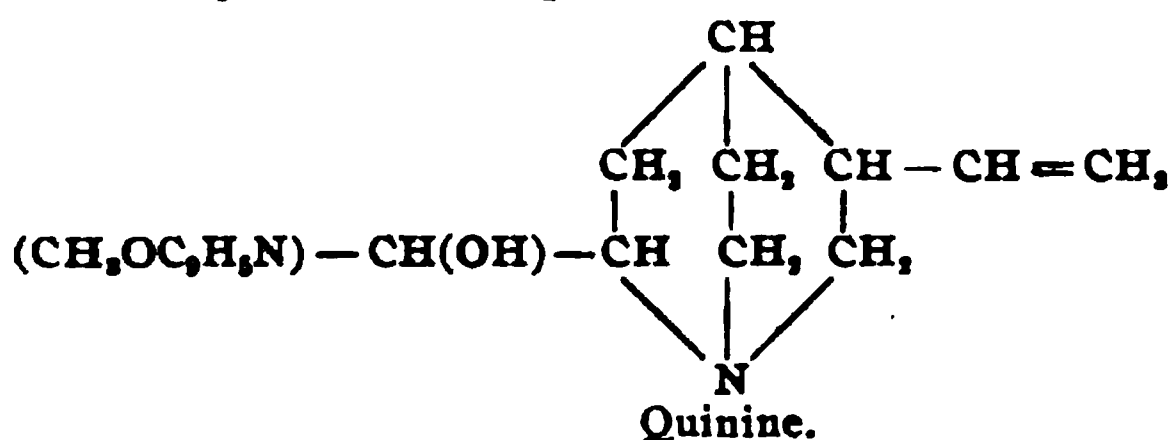
⁶ v. Miller and Rohde, *Ber.*, 33, 3214, 3220 (1900).

⁷ *Ibid.*, 28, 1056 (1895).

⁸ Rabe, *Ann.*, 364, 334 (1909); 373, 88, 92 (1910).



This peculiar molecular rearrangement to which cinchonine is subject at higher temperatures is not confined to this alkaloid. Other cinchona alkaloids¹ under similar conditions experience a like change. Thus, quinine, after prolonged boiling with acetic acid, is converted into a poisonous isomer, quinotoxine. The change in this case may be represented by the following formulas:



Quite remarkable is the change in physiological properties experienced by the cinchona alkaloids after they have undergone this molecular rearrangement. Both cinchonine and quinine lose entirely their characteristic febrifugal action and become intensely poisonous. On this account, as has already been indicated, v. Miller and Rohde gave to the new products the names cinchotoxine and quinotoxine and likened their poisonous action to that of digitoxin, the highly poisonous constituent of digitalis leaves. According to the recent investigations of Hilde-

¹ v. Miller and Rohde, *Ber.*, 28, 1056 (1895).

brandt,¹ the specific action of cinchotoxine in warm-blooded animals is to induce violent convulsions, resulting in death if the dose is sufficiently large. The action of quinotoxine is similar, although less in intensity.

According to this investigator, the toxicity of cinchotoxine and quinotoxine is largely to be ascribed to the presence of the imide group in the molecule.

In the administration of the salts of cinchonine and of quinine as a febrifuge, physicians² not infrequently report cases in which the action of the drugs appears to be abnormal. Such abnormal action, if accounted for at all, has been generally ascribed to some idiosyncrasy of the patient. The thought occurred to me some time ago that the toxic action of cinchonine and quinine might be due to the formation in the system of small quantities of cinchotoxine and quinotoxine. With this thought in mind the following investigation was undertaken to determine with greater exactness the conditions under which cinchonine and quinine are converted into their poisonous isomers. The results obtained are significant. It has been found that acids of not too large dissociation constants, such as the organic acids, under suitable conditions, play a remarkable role as catalyzers in effecting the conversion of the cinchona alkaloids into their poisonous isomers. It has been found, furthermore, that these alkaloids give rise to their toxic isomers under conditions which may obtain in portions of the digestive tract, that under favorable conditions, indeed, partial conversion will take place at ordinary atmospheric temperatures.

Cinchotoxine.

1. *Preparation and Properties of Cinchotoxine.*—Cinchotoxine was prepared according to the method of v. Miller and Rohde³ by heating at the boiling temperature for thirty-five hours a mixture of ten grams of cinchonine, ten grams of glacial acetic acid, and one hundred and thirty cc. of water. The brownish red solution when cooled was treated with excess of sodium hydroxide and the light brown oil which separated was extracted with ether. Instead of drying the ethereal solution with solid potassium hydroxide, as did v. Miller and Rohde, it was found more advantageous to effect dehydration by treatment with calcium carbide. Unchanged cinchonine being practically insoluble in dry ether is precipitated (except traces) when the solution is dried. The excess of ether was then evaporated off in a stream of dry hydrogen. The cinchotoxine is left as a light brown oil, which when well cooled gradually solidifies to a crystalline mass. After recrystallization from dry ether, the sub-

¹ Hildebrandt, *Archiv. fur. Ex. Path. u. Pharm.*, 59, 127 (1908).

² We are indebted to Dr. F. R. Woolsey, of Berkeley, for report on a number of these cases.

³ v. Miller and Rohde, *Ber.*, 28, 1064 (1895).

stance melts with preliminary softening, as given by v. Miller and Rohde, at 58–59°.

The crystals give the characteristic reddish-purple coloration with an alkaline solution of diazobenzene sulfonic acid¹ and with nitrobenzene containing in solution dinitrothiophene.²

A few of the salts of cinchotoxine are described in the literature.³ The hydriodide, $C_{19}H_{22}N_2O.HI$, was prepared by neutralizing cinchotoxine with hydriodic acid. The salt as recrystallized from alcohol is obtained in large brown prisms. A nitrogen determination led to the following results:

0.3 gram substance; 17.7 cc. N_2 at 24° and 755.5 mm.

Calculated for $C_{19}H_{22}N_2O.HI$: N, 6.65; found, 6.6%.

The following salts prepared by neutralizing cinchotoxine with the corresponding acid and purified by recrystallization from alcohol were not analyzed:

Cinchotoxine sulfate, white, crystalline plates, m. p. 56°.

Cinchotoxine lactate, colorless plates, m. p. 56°.

Cinchotoxine propionate, white plates, m. p. 59°.

2. *Conversion of Cinchonine into Cinchotoxine at 100°*.—In the conversion of cinchonine into cinchotoxine by fusion of the bisulfate, Pasteur employed temperatures of 160° and above. Similarly, Hesse effected the transformation at temperatures above 130°. As we have seen, a practically quantitative conversion of the alkaloid into its poisonous isomer is brought about by heating cinchonine with acetic acid at 100°. The suggestion naturally presents itself that possibly the particular acid concerned may have some influence upon this molecular change. To determine this point a series of experiments was carried out in which like quantities of cinchonine were heated at 100° for the same length of time with excess of different acids and the actual amount of conversion produced was determined by isolating and weighing the cinchotoxine formed. It was found that some change was effected in the case of all the acids used, but that the amount of conversion varied between the widest limits. Organic acids such as acetic and propionic gave almost quantitative change, while in the case of the highly ionized mineral acids, such as hydrochloric acid, the cinchotoxine produced was simply a trace.

These results seemed to indicate the possibility, on the one hand, of a strong catalyzing influence on the part of certain organic acids, and on

¹ Penzoldt and Fisher, *Ber.*, 16, 657 (1883). v. Miller and Rohde, *Ibid.*, 28, 1058 (1895).

² v. Meyer, *Ibid.*, 17, 2778 (1884); 18, 533 (1885). v. Miller and Rohde, *Ibid.*, 33, 3223 (1900).

³ Hesse, *Ann.*, 178, 256 (1875). Roques, *Bull. soc. chim.*, [3] 13, 1007 (1895). Howard, *J. Chem. Soc.*, 25, 102 (1872).

the other hand an inhibiting influence due to the concentration of the hydrogen ions. In order that further light might be thrown upon these points, a series of experiments was carried through with different acids in solutions of known concentration with respect to the hydrogen ion. To determine the concentration of the hydrogen ions, recourse was had to the colorimetric scheme proposed by E. Salm,¹ his series of standard solutions varying from 2 *N* hydrogen ion to 1×10^{-10} *N* hydrogen ion being used as a basis of comparison. The following eight indicators were employed in determining the normality of the hydrogen ion: cochineal, hematein, congo red, litmus, methyl orange, methyl violet, *p*-nitrophenol, phenacetolin, phenolphthalein, rosolic acid and sodium alizarin sulfonate.

In the experiments whose results are tabulated below, the mode of procedure was uniformly as follows: The acid was added to 5 g. of cinchonine in 65 cc. of water. The mixture was then heated for 48 hours on an electric heater at 98–102°. The cooled solution was thereupon treated with excess of sodium hydroxide and the cinchotoxine and unchanged cinchonine extracted with ether, care being taken to follow like conditions of procedure in each case. After the ethereal solution had been freed from moisture and all but traces of dissolved cinchonine by treatment with calcium carbide, the ether was evaporated off and the weight of the dry residue determined, when it had become constant. This residue presented, in every case in which there was sufficient for examination, the characteristic properties of cinchotoxine.

During the process of heating, the solutions in all cases were more or less colored from the formation of resinous matter insoluble in ether. In general those solutions were least colored in which the lesser amount of cinchotoxine was formed. In those cases in which practically a quantitative conversion to cinchotoxine was effected slight quantities of an oily resin insoluble in ether were frequently obtained. These, in many cases, contained traces of unchanged cinchonine.

It should be stated that the results following are to be regarded only as roughly quantitative, the object being to determine the influence of the reagent in question on the general course of the reaction. Furthermore, the colorimetric scheme of Salm is open to criticism as to its accuracy when used in the presence of such substances as the salts of cinchonine. The observed concentrations of the hydrogen ions are, consequently, to be regarded as presenting only approximate values.

The results obtained, however, clearly reveal a most remarkable case of catalysis concerning which I presented a preliminary report before the section in organic chemistry of the 42nd general meeting of the American Chemical Society, held in San Francisco, July, 1910.²

¹ *Z. physik. Chem.*, 57, 471 (1906).

² In November, 1910, Rabe reports (*Ber.*, 43, 3308) certain work carried out

TABLE I.

Acid.	Ratio of cinchonine (1 mol.) to equivalent of acid.	Approximate concentration of hydrogen ion.	Dissociation constant K.	Cinchotoxine formed. Grams.	Unchanged cinchonine recovered. Grams.	Amount of conversion.
1 Hydrochloric.....	1 : 4	1×10^{-1}	None	4.7	None
2 Oxalic.....	1 : 4.5	1×10^{-2}	0.1	4.7	2.0%
3 Dichloroacetic.....	1 : 3.5	1×10^{-2}	5.1	0.1	4.8	2.0%
4 Monochloroacetic...	1 : 3	$\left\{ \begin{array}{l} 1 \times 10^{-2} \\ -1 \times 10^{-2} \end{array} \right\}$	0.155	0.5	4.1	10.0%
5 Tartaric.....	1 : 4	1×10^{-2}	0.097	4.6	None	Quantitative
6 Malic.....	1 : 4.5	1×10^{-2}	0.0395	4.7	"	"
7 Formic.....	1 : 8	1×10^{-2}	0.0214	4.6	"	"
8 Lactic.....	1 : 4	1×10^{-2}	0.0138	4.7	"	"
9 Citric.....	1 : 4	$\left\{ \begin{array}{l} 1 \times 10^{-2} \\ -1 \times 10^{-4} \end{array} \right\}$	4.7	"	"
10 Acetic.....	1 : 20	1×10^{-4}	0.0018	4.6	"	"
11 Acetic.....	1 : 5	1×10^{-4}	0.0018	4.7	"	"
12 Hydrochloric.....	1 : 1.2	1×10^{-4}	0.12	4.7	2.4%
13 Hydrochloric (Cinchonine hydrochloride).....	1 : 1	1×10^{-6}	0.15	4.75	3.0%
14 Sulfuric (Cinchonine sulfate).....	1 : 1	1×10^{-6}	0.2	4.6	4.0%
15 Tartaric (Cinchonine tartrate, 5 g. of cinchonine in 175 cc. of solution)	1 : 1	1×10^{-6}	0.5	4.2	10.0%
16 Tartaric (Cinchonine tartrate, 5 g. of cinchonine in 175 cc. of solution) and sodium potassium tartrate (5 mol.)....	1 : 1 : 10	0.5	4.3	10.0%

From these experiments it is seen that cinchonine gives rise to cinchotoxine when salts of the alkaloid either with or without excess of acid are heated in aqueous solution at 98–102°. With excess of acid the speed of conversion, or the amount of change in unit time, in general increases with acids of decreasing dissociation constant. With such acids as hydrochloric, oxalic, dichloroacetic and monochloroacetic, the rate of conversion is comparatively slow, nor is this rate of conversion much affected by lowering the concentration of the hydrogen ion of a strong acid such as hydrochloric, as is shown in Expt. 12. A similar slow rate of con-

by McMillan on the accelerating action of weak acids, such as many of the organic acids, on the conversion of cinchonine into cinchotoxine. He has, apparently, overlooked the fact that four months before I brought out the same points, in addition to others, in my preliminary report before the American Chemical Society in San Francisco and that an abstract of said report was published in the October number of *Science*, 32, 486 (1910).

version obtains in the case of the neutral salts, such as the hydrochloride and sulfate. With excess of acids of small dissociation constant such as tartaric, malic, formic, lactic, citric, and acetic, the rate of change is enormously increased so that within 48 hours, under the conditions of the experiment, the conversion is quantitative. This increase in speed of conversion, apparently, does not take place in case of the monacid salts of cinchonine with these acids even in the presence of excess of the neutral salts of such acids, as is shown in Expts. 15 and 16.

In order that more definite information might be obtained regarding the comparative speed of conversion, experiments were carried out whose results are recorded in Table II. 5 g. of cinchonine were used in each case with 5 equivalents of acid in 65 cc. of water.

TABLE II.

Acid.	K.	Time of heating.					
		6 hours.		24 hours.		48 hours.	
		Cincho- toxine formed. Grams.	Cincho- nine recovered. Grams.	Cincho- toxine formed. Grams.	Cincho- nine recovered. Grams.	Cincho- toxine formed. Grams.	Cincho- nine recovered. Grams.
1 Hydrochloric.....	None	4.6
2 Monochloracetic..	3.155	0.2	4.5	0.3	4.4
3 Tartaric.....	0.097	1.7	3.0	4.5	0.2	4.7	None
4 Acetic.....	0.0018	2.4	2.2	4.7	None

The enormous increase in the speed of conversion observed in passing from monochloracetic to tartaric acid seems remarkable in view of the little difference between the dissociation constants of these acids. But these results are in accord with those found in Table I, where, as is seen, a marked change occurs at this point. In the case of the acetic acid, as may be noted, conversion to the extent of 50% occurs within 6 hours.

TABLE III.

Acid.	Ratio of cincho- nine (1 mol.) to equivalent of acid.	Approximate concentration of hydrogen ion in the solution.	Cincho- toxine formed. Grams.	Unchanged cinchonine recovered. Grams.	Amount of conversion.
1 Hydrochloric.....	1 : 4	1×10^{-1}	None	4.7	None
2 Hydrochloric and acetic..	1 : 4 : 5	1×10^{-1}	0.2	4.8	4.0%
3 Dichloracetic.....	1 : 3.5	1×10^{-2}	0.1	4.8	2.0%
4 Dichloracetic and acetic..	1 : 3.5 : 5	1×10^{-2}	0.18		3.6%
5 Hydrochloric.....	1 : 1.2	1×10^{-4}	0.12	4.7	2.4%
6 Hydrochloric and acetic..	1 : 1.2 : 5	1×10^{-4}	4.2	...	84.0%
7 Hydrochloric (Cinchonine hydrochloride).....	1 : 1	1×10^{-6}	0.15	4.6	4.0%
8 Hydrochloric (Cinchonine hydrochloride) and so- dium dihydrogen phos- phate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$)..	1 : 1 : 4	1×10^{-6}	4.7	None	Quantitative

The catalyzing influence of the weaker acid appears also in the case of the *monacid* salts of cinchonine with the more strongly dissociated

acids, such as cinchonine hydrochloride. This is shown in the preceding results which were obtained under the same conditions of heating as those given in Table I.

As may be seen from these results when the strongly dissociated acid, such as hydrochloric, is present in sufficient quantity to form the diacid salt of cinchonine or is in excess of this amount, the less dissociated acid apparently exerts a weak catalytic action but the acceleration is practically negligible. If, however, the strongly dissociated acid is present only in sufficient quantity to form the monacid salt of cinchonine or is but slightly in excess of this quantity, presence of sufficient quantity of the less dissociated acid suffices to effect practically quantitative conversion of cinchonine into cinchotoxine within 48 hours. The rate of conversion is, consequently, apparently closely dependent upon the condition of the less basic or second nitrogen atom in the cinchonine molecule.

From these considerations it might be suggested that an explanation of this remarkable case of catalysis is to be sought under the phenomena of hydrolysis. As a study of the conditions of this conversion is being continued with the idea of more fully determining its nature, I wish for the present to withhold an interpretation of the reaction until further data is obtained.

3. *Conversion of Cinchonine into Cinchotoxine at 36°.*—The formation of cinchotoxine from cinchonine may be effected in the presence of the preceding catalyzing agents at temperatures as low as 36°, or at temperatures corresponding to those occurring in the body. The conversion at these temperatures is in every case slight—a matter which renders somewhat tedious the separation of the cinchotoxine from the unchanged cinchonine in attempting to determine the amount of the former produced. Fortunately a ready method for the detection of cinchotoxine is found in the two color tests already referred to, *viz.*, that with an alkaline solution of diazobenzene sulfonic acid and that with a solution of dinitrothiophene in nitrobenzene.

The Diazobenzene Sulfonic Acid Reagent.—This is most conveniently prepared by making a freshly saturated aqueous solution of the free acid. The solution to be tested is added to 2–3 cc. of the solution of the reagent, after the latter has been rendered alkaline by the addition of a little caustic soda. If cinchotoxine is present, the solution is colored within 5–15 minutes, the color varying from a light pink to a deep reddish violet, according to the amount of cinchotoxine present. The reaction is determined apparently by the presence in cinchotoxine of the carbonyl group, as it is yielded by aldehydes and, in general, somewhat less pronouncedly by ketones.¹

¹ Penzoldt and Fischer, *Ber.*, 16, 657 (1883). v. Miller and Rohde, *Ibid.*, 28, 1058 (1895).

This color test, unlike the other, may be used directly in testing the alkaline solution from which the cinchonine and cinchotoxine have been precipitated by the addition of an alkali. If much cinchotoxine has been formed, sufficient will remain in solution to give a distinct reaction. Small amounts, however, may escape detection in this application of the reagent.

The Dinitrothiophene Reagent.—This was prepared by dissolving dinitrothiophene in pure nitrobenzene (1 : 200). Ordinary impure nitrobenzene frequently contains sufficient dinitrothiophene to serve as an indicator. To 1–2 cc. of the reagent is added a few drops of alcohol and then the substance to be tested. Presence of cinchotoxine is indicated by a color change varying from light reddish yellow to a deep wine-red (with at first a distinct violet tint) according to the amount of cinchotoxine present. Brunner¹ considered the reaction to depend upon the imide group in cinchotoxine, but it seems more reasonable to consider it as due to the pronounced basic character of this substance, since the reaction is given vigorously by such strong bases as sodium hydroxide and triethylamine, and much less vigorously by weaker bases such as aniline and ethyl aniline. In employing the dinitrothiophene reagent, the cinchotoxine was freed from sodium hydroxide and all but traces of co-precipitated cinchonine by extracting with ether. The ethereal solution, after dehydration with calcium carbide, was evaporated to dryness and the residue taken up with a little ether, and was added directly to 2–4 drops of the reagent together with a little alcohol.

To determine the influence of the various acids upon cinchonine at lower temperatures, a series of experiments was carried out at 36° similar to those conducted at 100°. In these experiments the method of procedure was in general like that followed in the preceding case. The bases were precipitated with excess of sodium hydroxide and both the alkaline solution and the unchanged cinchonine carefully extracted with ether. The cinchotoxine obtained on evaporation of the dried solution was freed from traces of cinchonine by solution in a little dry ether. It was thus possible to detect and to isolate even traces of cinchotoxine from a large quantity of unchanged cinchonine. The cinchotoxine obtained at the lower temperature gives the vigorous color reactions with dinitrothiophene in nitrobenzene and with diazobenzene sulfonic acid and in all its properties is identical with that obtained at the higher temperature.

In making the colorimetric tests, the cinchotoxine was ordinarily dissolved in a little pure, dry ether and this solution was added to the reagent in question. The ether employed throughout the work was carefully freed from vinyl alcohol² and other impurities which are found in

¹ v. Miller and Rohde, *Ber.*, 33, 3223 (1900).

² Poleck, Thümmel, *Ibid.*, 22, 2863 (1889).

ordinary ether and which would give color reactions with an alkalin solution of diazobenzene sulfonic acid.

In the experiments (excepting the last) recorded in the following table, the acid in each case was dissolved in 10 cc. of water and the aqueous solution added to $2\frac{1}{2}$ g. of cinchonine. The temperature was then maintained at 36° for 48 hours:

TABLE IV.

Acid.	Ratio of cinchonine (1 mol.) to equivalent of acid.	Cinchotoxine formed.	Approximate per cent of conversion.	Remarks.
1 Hydrochloric.....	1 : 5	None	.	Solution scarcely colored by heating
2 Hydrochloric.....	1 : 5	"		Solution scarcely colored by heating
3 Sulphuric (Cinchonine bisulfate).....	1 : 2	"		
4 Formic.....	1 : 6	Slight amount		Solution strongly colored by heating
5 Acetic.....	1 : 5	" (0.02 g.)	0.8	
6 Acetic.....	1 : 5	" (0.025 g.)	1.0	
7 Propionic.....	1 : 5	" (0.04 g.)	1.6	
8 Malic.....	1 : 7	"		
9 Lactic.....	1 : 4	" (about 0.006 g.)	0.2	
10 Citric.....	1 : 8	Very slight amount		Solution somewhat colored by heating
11 Sulfuric (Cinchonine sulfate; 4 g. in 30 cc. of water) and acetic.	1 : 1 : 5	Slight amount (about 0.005 g.)	0.2	

As is seen, the results accord in general with those obtained with the same acids at 100° , the differences being those of degree rather than of character. The conversion, however, is slight, in no case reaching 2%.

The following results were obtained by the action of acetic acid and hydrochloric acid and mixtures of these two acids, in each case on 2 g. of cinchonine in 10 cc. of water, the temperature being maintained at 36° for 48 hours:

TABLE V.

Acid.	Ratio of cinchonine (1 mol.) to equivalent of acid.	Cinchotoxine formed.
1 Acetic.....	1 : 10	Small amount (about 0.03 g.)
2 Acetic.....	1 : 5	" (about 0.01 g.)
3 Acetic and hydrochloric.....	1 : 5 : 1.6	" (less than 0.006 g.)
4 Acetic and hydrochloric.....	1 : 2.5 : 5	None
5 Hydrochloric.....	1 : 5	None
6 Hydrochloric.....	1 : 10	None

These results likewise are in perfect accord with those obtained at 100°. Hydrochloric acid, which at the higher temperature shows no change, at the lower temperature gives none detectable. Acetic acid, which at the higher temperature gave a large conversion, shows here the same general catalyzing action. Here, as at the higher temperature, with a mixture of the two acids, an excess of hydrochloric acid inhibits the catalyzing action of the acetic acid, while in the presence of only a little hydrochloric acid (less than 2 acid equivalents to the cinchonine molecule), a partial catalysis takes place.

4. *Effect of Dilution on the Conversion of Cinchonine to Cinchotoxine.*—The catalyzing influence of the organic acid is not destroyed even on large dilution as is shown in the following results, which were obtained by maintaining the temperature at 36° for 48 hours:

TABLE VI.

	Acid.	Amount of cinchonine. Grams.	Water. cc.	Percentage of cinchonine in the solution.	Cinchotoxine formed. Gram.	Per cent conversion.
1	Acetic (7.4 cc., 99.9%).....	10.0	20	26.3	0.1	1.0
2	Acetic (2 cc., 99.9%).....	2.5	10	17.1	0.02	0.8
3	Acetic (2 cc., 99.9%).....	2.0	200	0.98	0.0075	0.37

5. *Effect of Duration of Time on the Conversion of Cinchonine into Cinchotoxine.*—The amount of cinchotoxine formed from a given quantity of cinchonine at 36° by the action of organic acids apparently increases but slowly with continuance of the action. Appreciable conversion is usually easily shown within 24 hours or less. Prolonged maintenance of temperature leads to the formation of considerable resin and it is probable, as will be shown later, that the cinchotoxine is in part polymerized into this.

The following experiments were carried out at 36°, the acid used being acetic:

TABLE VII.

Amount of cinchonine. Grams.	Ratio of cinchonine (1 mol.) to equivalent of acid.	Water. cc.	Time.	Cinchotoxine formed.	Approximate conversion. Per cent.
2	1 : 5	10	48 hrs.	0.02	1.0
2	1 : 5	10	15 days	0.085	4.2
20	1 : 5	100	3.5 mo.	about 1 g.	5.0

6. *Action of Organic Substances other than Acids upon Cinchonine.*—As shown by Howard,¹ cinchonine, when heated with glycerine to 180° and above this temperature, is converted into cinchotoxine. The influence of neutral substances at lower temperatures is consequently of interest.

Four grams of cinchonine were heated in a solution of absolute alcohol at the temperature of the boiling alcohol for 48 hours. The solution, which remained perfectly clear and colorless, was cooled and separated

¹ Howard, *J. Chem. Soc.*, 25 102 (1872).

from the excess of cinchonine, which crystallized out. The residue remaining on evaporation of the alcohol was found to be free from cinchotoxine.

The effect of alcohol upon a salt of cinchonine was determined by heating 5 g. of cinchonine hydrochloride dissolved in a mixture of equal parts of water and absolute alcohol, the solution being maintained at the temperature of boiling for 48 hours. A small amount (about 0.04 g.) of cinchotoxine was formed, but the quantity was less than that obtained from heating cinchonine hydrochloride in aqueous solution alone at about the same temperature for the same length of time.

Experiments carried out with cinchonine in acetone, chloroform, and mixtures of chloroform and alcohol gave no evidence of the formation of cinchotoxine. These solvents, consequently, do not act as catalyzers under such conditions to effect the conversion of cinchonine into cinchotoxine.

7. *The Action of Sunlight on the Salts of Cinchonine.*—The salts of cinchonine and of the cinchona alkaloids in general are profoundly affected by the sunlight—a matter which was noted by Pasteur¹ as early as 1853 and to which later Hesse² called attention. These investigators suspected that the changes produced were similar to those effected at elevated temperatures, but they failed to confirm their suspicions.

A study of the behavior of the salts of cinchonine under the influence of sunlight discloses the fact that the changes produced are of the same nature as those already considered. Three solutions of 100 cc. each containing in each case 1 g. of cinchonine dissolved in four molecules of hydrochloric, acetic and citric acids, respectively, were exposed to the direct action of the sunlight. Within eight hours the solutions containing the cinchonine acetate and citrate were deep brown in color from the formation of resinous matter, while the solution containing the hydrochloride was unchanged. After twenty hours' exposure, the brown of the first two had deepened in intensity, while the last solution had only begun to show a trace of color. Precipitation of the cinchonine, extraction with ether, etc., as before, revealed the presence of traces of cinchotoxine in the case of the acetic acid and the citric acid, but none in the case of the hydrochloric acid.

Solutions of the salts of cinchonine are affected in the same way by diffused light, although in this case the action is naturally much slower. Solutions of the alkaloid with the above acids were allowed to stand in diffused light at ordinary temperatures for about 60 days. The color changes corresponded with those obtained by the more rapid action of the direct sunlight.

¹ Pasteur, *Compt. rend.*, 37, 110 (1853).

² Hesse, *Ann.*, 166, 275 (1873).

The action of sunlight upon the salts of cinchonine results in the formation of much resinous matter. It seems probable that this is derived not directly from the alkaloid but from cinchotoxine formed as an intermediate product. Salts of the latter base are even more sensitive to sunlight than those of cinchonine. Like those of cinchonine, the salts of cinchotoxine with organic acids in the presence of excess of acid are converted into resinous matter in the sunlight much more rapidly than those with such acids as hydrochloric. Thus, a solution of cinchotoxine in acetic acid exposed to the sunlight becomes deep brown in color before a corresponding solution of the alkaloid in hydrochloric acid is much affected.

8. *Conversion of Cinchonine into Cinchotoxine, Apparently not Reversible.*—The fact that prolonged action of the organic acids at 36° but slowly increases the amount of cinchotoxine formed naturally leads to the inference that the action is reversible, a condition of equilibrium having been approached. The quantitative conversion at 100° , however, does not favor this view. Furthermore, previous attempts¹ as well as attempts made by myself to reverse the action have thus far been unavailing. It is possible that we are dealing here with a case of false equilibrium²—a matter, however, which cannot be determined without a more extensive study of the conditions underlying this molecular change.

A study of the possible reversal of cinchotoxine to cinchonine is much complicated by the large number of stereoisomeric substances which may arise from cinchonine because of the existence in the molecule of four dissimilar asymmetric carbon atoms (see formula of Rabe). Indeed, nearly twenty such isomers have been described as obtained from cinchonine by the action of acids or alkalies under varying conditions of temperature.³ It may be that future study will decrease (as more recent investigation appears to be doing) the number of these isomers by showing that some of them are identical with one another. The number of isomers actually possible is naturally increased, if one includes with these cinchotoxine and the possible stereoisomers of this substance.

While the direct reversal of cinchotoxine to cinchonine appears improbable, it is interesting to note that Rabe⁴ has recently, by an indirect method, succeeded in converting the former substances into the latter, thus solving one step in the partial synthesis of cinchonine.

¹ Koenigs, *Ber.*, 40, 2875 (1907).

² Duhem-Burgess, "Thermodynamics and Chemistry," 1903, p. 369.

³ Hesse, *Ann.*, 205, 330 (1880); 227, 153 (1885); 243, 131 (1888); 260, 213 (1890); 266, 245 (1891); 267, 142 (1892); 276, 88 (1893). Skraup, *Ann.*, 201, 291 (1880); *Ber.*, 25, 2909 (1892); *Monatsh.*, 12, 431 (1891); 18, 411 (1897); 20, 571, 585 (1899); 21, 512 (1900); 22, 171, 253, 1083, 1097 (1901). Skraup and Zwerger, *Monatsh.*, 21, 535 (1900); 23, 455 (1902). Zwerger, *Monatsh.*, 24, 119 (1903). Comstock and Königs, *Ber.*, 20, 2510 (1887), and many others.

⁴ Rabe, *Ber.*, 44, 2088 (1911).

Quinotoxine.

9. *Preparation and Properties of Quinotoxine.*—Quinotoxine, or quini-cine, bears to quinine (the methoxyl derivative of cinchonine) the same relation that cinchotoxine bears to cinchonine. It was first obtained by Pasteur¹ in 1853 by heating quinine with dilute sulfuric acid to 120–130°. In general, the conversion of quinine into its poisonous isomer has been effected under conditions quite parallel with those under which cinchonine yields cinchotoxine.²

Quinotoxine was prepared from quinine by the same general process used in obtaining cinchotoxine from cinchonine, *viz.*, the heating of the alkaloid with acetic acid for 35 hours at 100°. As obtained from its ethereal solution, it forms a yellowish brown oil, which does not crystallize. On standing in the air it is, after some time, converted into an amorphous resinous mass, having a rough melting point near 60°. It is slightly soluble in water, readily so in alcohol, ether, and chloroform. Like cinchotoxine, quinotoxine contains ketone oxygen and an imide group; it responds like that compound to the color tests with diazobenzene sulfonic acid and dinitrothiophene in nitrobenzene; and in its reactions in general, it shows itself to be the analog of cinchotoxine.

10. *The Conversion of Quinine into Quinotoxine at 100°.*—The catalyzing action of various acids upon quinine at 100° closely resembles the corresponding action of these acids upon cinchonine. The experiments whose results are given in the following table were carried out as in the former case (see page 505). Since quinine, unlike cinchonine, is somewhat soluble in dry ether (approximately 1 part in 18 parts at 18°), the separation of the quinotoxine from unchanged quinine presents additional difficulties. The results obtained are consequently open to a greater degree of experimental error, particularly in cases where much quinine remained unchanged. A moment's consideration of these results, however, shows their close accord with the like results obtained in the case of cinchonine:

TABLE VIII.

Amount of quinine used, 5 g.; temperature, 98–102°; time of heating, 48 hours.

Acid.	Ratio of quinine (1 mol.) to equiv- alent of acid.	Dissociation constant. K.	Quinotoxine formed. Grams.
Hydrochloric.....	1 : 4	None
Formic.....	1 : 8	0.0214	4.5
Lactic.....	1 : 4	0.0138	4.6
Acetic.....	1 : 5	0.0018	4.5

11. *The Conversion of Quinine into Quinotoxine at 36°.*—In the presence

¹ Pasteur, *Compt. rend.*, 37, 110, 166 (1853); *Jahrb.*, 1853, 473.

² Hesse, *Ann.*, 166, 277 (1873); 243, 148 (1888). v. Miller and Rohde, *Ber.*, 33, 3228 (1900).

of the ordinary organic acids, such as formic, propionic, butyric and lactic, quinine like cinchonine yields within 48 hours, at 36°, an appreciable quantity of its poisonous isomer, quinotoxine. In the presence of excess of sulfuric or hydrochloric acid under the same conditions there is no detectable conversion.

In a few cases the quinotoxine formed at 36° was freed from all but traces of unchanged quinine, but the difficulty of separating small quantities of the substance from large amounts of unchanged base rendered the results of little quantitative value. The quinotoxine obtained, however, possesses all the properties of that formed at 100° and the degree of conversion is of like order to that occurring in the case of cinchonine under the same conditions.

12. *The Employment of the Cinchona Alkaloids in Medicin.*—From the results of these investigations it is very clear that cinchotoxine and quinotoxine may be formed in small quantities in the system during the administration of the salts of cinchonine or of quinine. As shown by Hildebrandt,¹ these isomers have no febrifugal properties while their poisonous character is most pronounced. Although the amount of conversion would apparently be slight, yet the question is naturally raised as to whether the administration of the cinchona alkaloids under these circumstances becomes in any way a menace to the health of the patient. While Hildebrandt has studied the action of cinchotoxine and quinotoxine upon the lower warm-blooded animals, such as rabbits and cats, unfortunately, we have no data regarding their action upon the human system, unless the so-called abnormal behavior of the salts of cinchonine and quinine be regarded as furnishing such.

In medicin, cinchonine and quinine are sometimes administered in the form of the free alkaloid; more frequently, however, in the form of their salts. Doses of varying quantity are given: from 1–2 grains (0.06–0.12 g.) as a tonic, to 15–30 grains (1–2 g.) as an antiperiodic. The possibility of a 1–2% conversion of the alkaloids into their poisonous isomers in the presence of some such catalyzing agent as acetic acid, malic acid, citric acid, or lactic acid follows naturally from the experimental evidence adduced. Foods such as sour milk, acid fruits and the like, would, consequently, favor such conversion.

It seems most probable, from these considerations, that the abnormal behavior of the salts of cinchonine or of quinine, when these alkaloids are administered as a medicin, finds its explanation in their partial conversion under favorable conditions, into their poisonous isomers.

13. *Summary of Results.*—1. Cinchonine and quinine, when heated at 98–102° in the form of their salts in aqueous solution, either with or

¹ Hildebrandt, *Archiv. Exper. Path. Pharm.*, 59, 127 (1908).

without excess of acid, give rise to their poisonous isomers, cinchotoxine and quinotoxine.

2. In a general way, the rate of conversion of these alkaloids in the presence of acids increases with acids of decreasing dissociation constant. By changing the nature of the acid used and consequently the concentration of the hydrogen ion, the rate of conversion can be caused to vary between the widest limits. Thus, in the presence of excess of such acids as hydrochloric the rate of conversion may be so reduced as to give no detectable change after heating at $98-102^{\circ}$ for 48 hours. On the other hand, in the presence of acids of small dissociation constant, such as acetic and propionic, the rate of conversion may be so accelerated under the same conditions as to lead to quantitative conversion in 24 hours.

3. The rate of the conversion of these alkaloids when heated at $98-102^{\circ}$ in their monacid salts with various acids and in their diacid salts with strong acids is slow. The rate of this conversion in the case of the monacid salts is enormously increased by the introduction of an acid of small dissociation constant such as acetic acid. In the case of their diacid salts with the strong acids, however, such introduction of the weak acid is of but slight effect.

4. Neutral substances, such as alcohol and chloroform, do not, under ordinary conditions, act as catalyzers in accelerating the conversion of these alkaloids into their isomers.

5. The salts of cinchonine and quinine undergo similar conversion when kept in solution at a temperature of 36° , the only noteworthy difference from that effected at $98-102^{\circ}$ being the diminished rate of conversion. Thus, with such acids as hydrochloric and sulfuric, the conversion in 48 hours is too slight to be detected, while in the presence of the little dissociated organic acids, such as acetic and propionic, a conversion closely approaching 2% has been observed within the same length of time.

6. In the sunlight at ordinary temperatures the salts of cinchonine and quinine in solution undergo changes similar to those effected by rise of temperature. The cinchotoxine and quinotoxine, in this case as at more elevated temperatures, give rise to resinous matter, which colors the solutions.

7. The conditions under which cinchotoxine and quinotoxine are produced indicate the possibility of the formation of these substances in the body in the administration of cinchonine and quinine as remedial agents and consequently afford a reasonable explanation of cases of so-called "quinine poisoning."

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY,
No. 202.]

RESEARCHES ON QUINAZOLINES (TWENTY-NINTH PAPER). A
FURTHER STUDY OF THE STILBAZOLES, HYDRA-
ZONES AND SCHIFF BASES OF THE
4-QUINAZOLONE GROUP.¹

BY MARSTON TAYLOR BOGERT AND GEORGE DENTON BEAL.

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Since the appearance of our recent paper on this subject,² the work has been continued and the additional results are here recorded.

In the condensation of aldehydes with α -methyl pyridines or quinolines, the alkines usually form easily and in some cases are so stable that considerable difficulty is experienced in dehydrating them to stilbazoles.³ With the quinazolone-aldehyde condensations, on the other hand, the alkines either do not form at all under the conditions of our experiments, or are so unstable that they immediately lose water and give the stilbazole, for we have been unable to isolate alkines in any of the reactions.

Further, while it has been shown⁴ that many stilbazoles add hydrogen or bromine readily, these reactions do not seem to run so smoothly with stilbazoles derived from 4-quinazolones. Hydriodic acid and red phosphorus evidently caused some reduction when brought into contact with 2-styryl-4-quinazolone, but no pure dihydro derivative could be isolated from the tarry product. The action of bromine upon this same styryl quinazolone gave rise to substitution and not to addition products. Limp-richt and Schwanert⁵ have observed a similar reaction with stilbene, and Dubke⁶ with α' - γ -dimethyl- α -stilbazole.

In addition to the compounds described in our previous paper, the preparation of the following new aldehyde condensation products is recorded here: 6-nitro-2-styryl-4-quinazolone, 2-*o*-nitrostyryl-4-quinazolone, *p*-nitrostyryl-4-quinazolone, 6-nitro-2-*p*-nitrostyryl-4-quinazolone, 2-styryl-3-ethyl-4-quinazolone, 2-styryl-3-phenyl-4-quinazolone, 2-styryl-3-*p*-tolyl-4-quinazolone, 2-styryl-3-benzyl-4-quinazolone, 2-styryl-3-*p*-anisyl 4-quinazolone, 2-styryl-3-*p*-phenetyl-4-quinazolone, 2-styryl-3- α -naphthyl-4-quinazolone, 2-styryl-3- β -naphthyl-4-quinazolone, 2-styryl-3-anilino-4-quinazolone, 2-*o*-hydroxystyryl-3-phenyl-4-quinazolone, 2-methylenedioxy-styryl-4-quinazolone, and 2-phenylbutadienyl-4-quinazolone.

¹ Read at the Washington Meeting of the Society, Dec. 29, 1911.

² Bogert, Beal and Amend, *THIS JOURNAL*, 32, 1654 (1910).

³ For a tabulation of the condensations carried out by Ladenburg and his co-workers, see Dierig, *Inaug. Diss.*, Breslau, 1902.

⁴ Baurath, *Ber.*, 20, 2719 (1887); 21, 818 (1888). Ladenburg and Kröner, *Ibid.*, 36, 119 (1903). Tietz, *Inaug. Diss.*, Breslau, 1909, and others.

⁵ *Ann.*, 145, 336.

⁶ *Ber.*, 27, 82 (1894).

The condensation was generally carried out by heating an equimolecular mixture of the aldehyde and quinazolone. If the reaction was practically complete, the melt was purified by crystallization from alcohol, or some other suitable solvent, decolorizing with bone-black if necessary, while if the condensation was but a partial one, water was added, the excess of aldehyde driven out with steam, and the residue purified by crystallization.

Most of the styryl quinazolones are pale yellow or nearly colorless, and crystallize in fluffy masses of short silky needles. Frequently they exhibit tribo-electric properties. Usually they are soluble in alcohol, chloroform or glacial acetic acid; less readily in ether, carbon disulfide or benzene; and practically insoluble in water. Those with a free hydrogen in position 3 dissolve easily in aqueous solutions of the caustic alkalis and are reprecipitated by carbon dioxide or acetic acid.

Attention was called in the previous paper to the fact that 2-methyl-3-amino-4-quinazolone when treated with aldehydes condenses first with the amino group, and that the methyl group also reacts only when the attacking aldehyde is benzaldehyde. At the time, we suggested that the hydrazone group formed in position 3 prevented the reaction of the 2-methyl group by steric interference. We have since learned that an anilino group in position 3 exerts a similar influence, the 2-methyl group again condensing only with benzaldehyde.

Moore¹ has found that Schiff bases containing the chromophore group $-N:CH-$, together with certain auxochrome groups (for example, the $-N(CH_3)_2$ group), often form colored salts with acids. The hydrochlorides of several of our new Schiff bases were prepared by suspending the bases in dry ether and passing in dry hydrochloric acid gas, but the colors of the salts thus formed were invariably no darker than those of the bases from which they were obtained.

Fural, citral, acetophenone, and pyruvic acid failed to condense with these 2-methyl or 2-methyl-3-amino-4-quinazolones. Experiments with glyoxal also gave negative results. With benzil and 2-methyl-3-amino-4-quinazolone, some condensation occurred but the yield was too small to fully identify the product. Wislicenus² succeeded in condensing quinaldine with oxalic esters, in presence of sodium alcoholates, but a similar reaction does not occur when 2-methyl-4-quinazolone is substituted for the quinaldine.

By direct nitration of 2-styryl-4-quinazolone, both a mono and a dinitro derivative result. The former was proven to be the 6-nitro compound by its synthesis from 6-nitro-2-methyl-4-quinazolone and benzaldehyde; and the structure of the dinitro derivative was similarly es-

¹ THIS JOURNAL, 30, 394, 1001 (1908); 32, 382 (1910).

² Ber., 30, 1479 (1897).

established by its synthesis from 6-nitro-2-methyl-4-quinazolone and *p*-nitrobenzaldehyde.

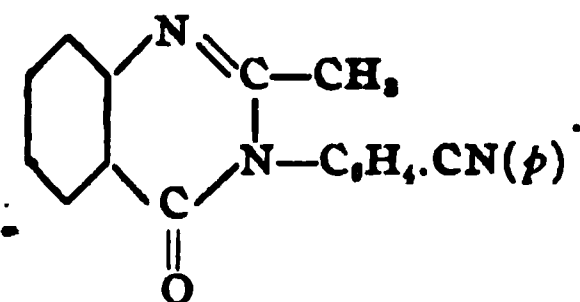
The amino group in 2-amino-4-quinazolone is decidedly inert. Although it can be acylated, it cannot be diazotized by ordinary methods, nor does it condense with aldehydes.

In the progress of the work, the following new quinazolones were prepared and studied: 2-methyl-3-*p*-cyanphenyl-4-quinazolone, 2-methyl-3-*p*-carboxyphenyl-4-quinazolone and its ethyl ester, 2-methyl-3-*p*-anisyl-4-quinazolone, 2-methyl-3-*p*-phenetyl-4-quinazolone, its sulfonic acid and the sodium salt of the latter, and 2-methyl-3-benzyl-4-quinazolone. Certain of these were prepared for the purpose of studying their physiological action upon animals. Thus, the *p*-phenetyl derivative, it was thought, might show antipyretic properties, but it proved to be too difficultly soluble. Sulfonation remedied the insolubility, but the sulfonated compound possessed no detectable therapeutic value. Similarly, the condensation product of *p*-aminobenzoic ester and acetanthranil was examined with reference to its power as a local anesthetic and found to be essentially inert. The details of these and other experiments on the physiological action of substances of this group will probably appear later in a separate paper.

Experimental.

I. Preparation of Quinazolones.

2-Methyl-3-p-cyanphenyl-4-quinazolone,



—*p*-Aminobenzonitrile and acetanthranil, in equimolecular proportion, were intimately mixed and the mixture heated for an hour at 150°. By crystallization of the reddish brown melt from alcohol, prisms were obtained of a faint pinkish cast, melting at 240° (cor.).

Calculated for $C_{16}H_{11}ON_3$: N, 16.09. Found: N, 16.37.

2-Methyl-3-p-carboxyphenyl-4-quinazolone, $HOOC.C_6H_4.N.CO.C_6H_4.N:CH_3$, was prepared from the above nitrile by boiling it with a 10% aqueous solution of potassium hydroxide until the evolution of ammonia ceased, cooling, and precipitating carefully with hydrochloric acid. The precipitated acid, washed with water, and recrystallized from dilute alcohol, forms short, yellowish needles, melting at about 259° (uncor.).

Calculated for $C_{16}H_{12}O_3N_2$: N, 10.00. Found: N, 10.41.

In recrystallizing this acid, prolonged boiling should be avoided, as

it tends to split out carbon dioxide from the acid and give the methyl phenyl quinazolone (m. p. 145°).

It may be recalled, in this connection, that Bogert and Klaber¹ found that anthranilic acid failed to condense with 4-nitroacetanthranil, although its methyl ester did.

Ethyl Ester.—The ester of the above acid was prepared from ethyl *p*-aminobenzoate and acetanthranil, by heating them together, in equimolecular proportion, for an hour at 150°, and crystallizing the brown melt from alcohol. Golden yellow prisms resulted which, on recrystallization, became practically colorless, and melted at 172–3° (cor.).

Calculated for $C_{18}H_{16}O_2N_2$: N, 9.09. Found: N, 9.43.

*2-Methyl-3-*p*-anisyl-4-quinazolone*, $\text{CH}_3\text{O.C}_6\text{H}_4.\text{N}.\text{CO.C}_6\text{H}_4.\text{N} : \text{C.CH}_3$, prepared in a similar manner, by heating together *p*-anisidine and acetanthranil for an hour at 150°, and purifying the product by crystallization from alcohol, forms colorless hexagonal prisms, melting at 170° (cor.).

Calculated for $C_{16}H_{14}O_2N_2$: N, 10.52. Found: N, 10.59.

*2-Methyl-3-*p*-phenetyl-4-quinazolone*, obtained in the same way, crystallizes from alcohol in needles of a faintly pinkish cast, melting at 148° (cor.), which darken gradually on standing in the air, and are freely soluble in alcohol or ether, but practically insoluble in water.

Calculated for $C_{17}H_{16}O_2N_2$: N, 10.00. Found: N, 10.11.

Monosulfo Acid.—The compound just described was sulfonated by stirring five grams of it into a mixture of 15 cc. concentrated and 30 cc. fuming sulfuric acid, and heating the mixture at 100° for two hours. The cooled solution was poured into 500 cc. ice water and the whole concentrated to half its original volume. On cooling, small grayish prisms separated, not melting at 300°.

Calculated for $C_{17}H_{16}O_5N_2S$: N, 7.77. Found: N, 7.70.

The sodium salt forms a gray powder, easily soluble in water, and having but little taste. It is unmelted at 300°.

2-Methyl-3-benzyl-4-quinazolone, $\text{C}_6\text{H}_5\text{CH}_2.\text{N}.\text{CO.C}_6\text{H}_4.\text{N} : \text{C.CH}_3$. — Equimolecular amounts of benzylamine and acetanthranil were mixed and the mixture heated half an hour at 150°. The melt was digested with cold water, to remove unchanged benzylamine, and with sodium carbonate solution, to eliminate any acetanthranilic acid. The residual quinazolone was purified by repeated crystallization from alcohol, and was thus obtained in colorless flakes, melting at 123° (cor.).

Calculated for $C_{16}H_{14}ON_2$: N, 11.20. Found: N, 11.11.

¹ THIS JOURNAL, 30, 814 (1908).

II. Condensations of Aldehydes with 2-Methyl-4-quinazolones containing no Primary Amino Groups. Simple Styryl Quinazolones.

2-Styryl-4-quinazolone, $\text{C}_6\text{H}_5\text{CH} : \text{CH.C} : \text{N.C}_6\text{H}_4.\text{CO.NH}$, has been described in our previous article. Its *hydrochloride* was prepared by adding concentrated hydrochloric acid to a saturated alcoholic solution of the quinazolone. Pale yellow needles separated which, when washed with alcohol and dried in a vacuum over concentrated sulfuric acid and solid potassium hydroxide, melted with decomposition at about 310° .

Calculated for $\text{C}_{16}\text{H}_{12}\text{ON}_2.\text{HCl}$: N, 9.84. Found: N, 9.99.

6-Nitro-2-styryl-4-quinazolone, $\text{C}_6\text{H}_5\text{CH} : \text{CH.C} : \text{N.C}_6\text{H}_3(\text{NO}_2).\text{CO.NH}$, was prepared by direct nitration of the above quinazolone (5 g.) with fuming (sp. gr. 1.52) nitric acid (50 cc.). The solution obtained was concentrated to half its original volume and then stirred into 300 cc. of ice water. The precipitated nitro compound was washed with water, then with alcohol, crystallized twice from glacial acetic acid, the crystals washed with alcohol and dried at 110° . Short, yellowish needles, melting at 323.5° (uncor).

Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$: N, 14.33. Found: N, 14.71.

That the nitro group in the above compound is in position 6 was proven by condensing benzaldehyde with 6-nitro-2-methyl-4-quinazolone, when the same substance was obtained.

Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$: N, 14.33. Found: N, 14.18.

This would appear to indicate that the benzene portion of the quinazoline nucleus nitrates more rapidly than the styryl group.

2-o-Nitrostyryl-4-quinazolone, $\text{O}_2\text{N.C}_6\text{H}_4.\text{CH} : \text{CH.C} : \text{N.C}_6\text{H}_4.\text{CO.NH}$.—Three grams each of *o*-nitrobenzaldehyde and 2-methyl-4-quinazolone were mixed and the mixture heated for two hours at 180° . The pulverized melt was extracted with boiling alcohol, to remove unchanged initial materials, and the residue crystallized from glacial acetic acid. Minute, yellowish needles resulted, melting at 300° (uncor.).

Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$: N, 14.33. Found: N, 14.24.

2-p-Nitrostyryl-4-quinazolone was prepared in the same way. It forms bright yellow, microscopic needles, melting at 350° (uncor.).

Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$: N, 14.33. Found: N, 14.30.

6-Nitro-2-p-nitrostyryl-4-quinazolone,

$\text{O}_2\text{N.C}_6\text{H}_4.\text{CH} : \text{CH.C} : \text{N.C}_6\text{H}_3(\text{NO}_2).\text{CO.NH}$.—Five grams of 2-styryl-4-quinazolone were nitrated with a mixture of 60 cc. fuming nitric and 30 cc. concentrated sulfuric acid. The solution was concentrated to half its original volume and poured into 250 cc. ice water, the dinitro compound separating as a curdy, orange precipitate. This precipitate was

filtered out, washed with water, and boiled with dilute potassium hydroxide solution, to remove unchanged initial materials. It was then again washed with water, and extracted twice with hot, glacial acetic acid, in which it is very difficultly soluble. The residue was washed with alcohol, dried at 110° and analyzed:

Calculated for $C_{16}H_{10}O_2N_4$: N, 16.56. Found: N, 16.60.

It is an orange-yellow solid, melting at 335° (uncor.). The same compound was obtained by heating together 6-nitro-2-methyl-4-quinazalone and *p*-nitrobenzaldehyde for four hours at 200° .

Calculated for $C_{16}H_{10}O_2N_4$: N, 16.56. Found: N, 16.56.

Monobromo-2-styryl-4-quinazolone.—On mixing glacial acetic acid solutions of bromine and 2-styryl-4-quinazolone, a yellow precipitate gradually separated. This was filtered out and crystallized from alcohol, giving yellow needles, which slowly decompose in the vicinity of 345° .

Calculated for $C_{16}H_{11}ON_2Br$: N, 8.56. Found: N, 8.75.

The filtrate from the above bromine derivative was found to contain hydrobromic acid, a further proof that substitution and not addition had occurred. The same monobrom derivative was obtained by using chloroform as the solvent and allowing the mixture to stand eight hours.

Dibromo-2-styryl-4-quinazolone was obtained when hot, glacial acetic acid solutions of the quinazolone and bromine were mixed, or when a chloroform solution of the two was allowed to stand for 24 hours. The precipitate obtained separates from hot alcohol as a colorless, amorphous solid, which turns brown at about 200° , but remains unmelted at 300° (uncor.).

Calculated for $C_{16}H_{10}ON_2Br_2$: N, 6.89. Found: N, 6.63.

The filtrate from the dibrom compound contains hydrobromic acid.

2-Styryl-3-methyl-4-quinazolone, $C_6H_5.CH : CH.C : N.C_6H_4.CO.N.CH_3$.—The preparation of this compound from 2,3-dimethyl-4-quinazolone and benzaldehyde is described in our previous paper.

We have since prepared it also from 2-styryl-4-quinazolone, by dissolving the latter in methyl alcohol, adding the calculated amounts of potassium hydroxide and then of methyl iodide, and heating with a reflux until the mixture showed a neutral reaction.

2-Styryl-3-ethyl-4-quinazolone, from 2-methyl-3-ethyl-4-quinazolone and benzaldehyde, heated in equimolecular proportion for an hour at 150° , and the crude product purified by crystallization from alcohol, forms clusters of pale yellow needles, melting at 125° (cor.).

Calculated for $C_{18}H_{16}ON_2$: N, 10.14. Found: N, 10.43.

2-Styryl-3-phenyl-4-quinazolone, from 2-methyl-3-phenyl-4-quinazolone and benzaldehyde at 180° , crystallizes from alcohol in short, lemon-yellow needles, melting at 201° (cor.).

Calculated for $C_{22}H_{16}ON_2$: N, 8.64. Found: N, 8.95.

2-Styryl-3-p-tolyl-4-quinazolone, from 2-methyl-3-*p*-tolyl-4-quinazolone and benzaldehyde at 180° , crystallizes from alcohol in fine, pale yellow needles, melting at 197° (cor.).

Calculated for $C_{22}H_{18}ON_2$: N, 8.28. Found: N, 8.30.

2-Styryl-3-benzyl-4-quinazolone, from 2-methyl-3-benzyl-4-quinazolone and benzaldehyde at 190° , crystallizes from alcohol in fine, pale yellow needles, melting at 142° (cor.), which mat together closely on the filter. Its formation has been used by us as a means of isolating and identifying the methyl benzyl quinazolone.

Calculated for $C_{22}H_{18}ON_2$: N, 8.28. Found: N, 8.37.

2-Styryl-3-p-anisyl-4-quinazolone, from 2-methyl-3-*p*-anisyl-4-quinazolone and benzaldehyde at 180° , crystallizes from alcohol in small, pale yellow needles, melting at 223° (cor.), which mat together closely.

Calculated for $C_{22}H_{18}O_2N_2$: N, 7.91. Found: N, 7.99.

2-Styryl-3-p-phenetyl-4-quinazolone, from 2-methyl-3-*p*-phenetyl-4-quinazolone and benzaldehyde at 160° , crystallizes from alcohol in minute, pale yellow crystals, melting at 204° (cor.).

Calculated for $C_{24}H_{20}O_2N_2$: N, 7.60. Found: N, 7.78.

2-Styryl-3- α -naphthyl-4-quinazolone, from 2-methyl-3- α -naphthyl-4-quinazolone and benzaldehyde at 160° , crystallizes from alcohol in short, yellowish needles, melting at 187° (uncor.).

Calculated for $C_{26}H_{18}ON_2$: N, 7.48. Found: N, 7.65.

2-Styryl-3- β -naphthyl-4-quinazolone, from 2-methyl-3- β -naphthyl-4-quinazolone and benzaldehyde at 160° , crystallizes from alcohol in short, yellowish needles, melting at 240° (uncor.).

Calculated for $C_{26}H_{18}ON_2$: N, 7.48. Found: N, 7.66.

2-Styryl-3-anilino-4-quinazolone, from 2-methyl-3-anilino-4-quinazolone and benzaldehyde at 180° , crystallizes from alcohol in dense, granular, cream colored crystals, melting at 217° (uncor.).

Calculated for $C_{22}H_{17}ON_2$: N, 12.38. Found: N, 12.62.

Attempts to condense 2-methyl-3-anilino-4-quinazolone with salicylaldehyde failed.

2-o-Hydroxystyryl-3-phenyl-4-quinazolone,

$HO.C_6H_4.CH : CH.C : N.C_6H_4.CO.N.C_6H_5$, from 2-methyl-3-phenyl-4-quinazolone and salicylaldehyde at 190° , crystallizes from alcohol in short, lemon-yellow prisms, melting at 270° (uncor.).

Calculated for $C_{22}H_{16}O_2N_2$: N, 8.23. Found: N, 8.38.

2-Methylenedioxytyryl-4-quinazolone,

$CH_2 \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} C_6H_3.CH : CH.C : N.C_6H_4.CO.NH$, from 2-methyl-4-quinazo-

lone and piperonal at 180° , crystallizes from alcohol (in which it is difficultly soluble) in minute needles of faint yellowish cast, melting at 305° (uncor.), which mat together, and show tribo-electric properties.

Calculated for $C_{17}H_{13}ON_2$: N, 9.59. Found: N, 9.76.

2-Phenylbutadienyl-4-quinazolone,

$C_6H_5.CH : CH.CH : CH.C : N.C_6H_4.CO.NH$, was prepared from cinnamic aldehyde and 2-methyl-4-quinazolone at 190° . The aldehyde was freshly distilled in vacuum before use, and that uncombined in the reaction was blown out with steam. The residual non-volatile yellow solid was dissolved in alcohol, the solution decolorized with bone-black, and from the filtrate, on cooling, the desired compound separated in long, yellow needles, which were purified by further crystallization from alcohol, and then melted at $257-8^{\circ}$ (uncor.).

Calculated for $C_{18}H_{14}ON_2$: N, 10.21. Found: N, 10.21.

III. Condensations of Aldehydes with Amino 2-Methyl-4-quinazolones.

In addition to the compounds described in our former article, the subjoined have been prepared and studied.

2-Styryl-3-acetamino-4-quinazolone was obtained both by the action of acetic anhydride upon the corresponding styryl amino quinazolone, and by the condensation of the methyl acetamino quinazolone with benzaldehyde. It crystallizes from alcohol in needles of a faint pinkish tinge, melting at 259° (uncor.).

Calculated for $C_{18}H_{16}O_2N_2$: N, 13.77. Found: N, 13.99.

As mentioned in the introductory portion of this paper, our attempts to condense the 2-methyl-3-amino-4-quinazolone with citral, fural, or glyoxal, proved futile.

2-Methyl-3-amino-4-quinazolone and Benzil.—An alcoholic solution of these two substances, on long boiling, deposited a very small amount of a difficultly soluble, yellow, granular solid, melting with decomposition at about 292° . Efforts to secure the condensation in other ways proved fruitless. The two substances were heated together dry and in various solvents, at ordinary pressure and in sealed tubes, alone and in presence of sodium alcoholates, traces of alkali, of acid, and of pyridine, but the experiments were unsuccessful. Only enough material was secured for a single analysis:

0.069 gram gave 7.8 cc. moist N at 24° and 766 mm.

Calculated for $C_{20}H_{14}N_4O$ $\begin{matrix} N : C-CH : C.C_6H_5 \\ | \qquad \qquad | \\ CO.N-N : C.C_6H_5 \end{matrix}$: N, 12.03. Found: N, 12.78.

More of the material and closer analytical results are needed before it can be said whether we really secured the product sought or not.

2-Amino-4-quinazolone and Benzaldehyde.—One gram of the quinazolone

was heated with a slight excess of benzaldehyde for an hour at 180°, but no condensation occurred.

The reaction is of interest, since we have shown that amino groups in positions 3 or 7 condense easily with benzaldehyde.

2-Methyl-4-quinazolone and Ethyl Oxalate.—Five grams of the dry quinazolone, a similar amount of ethyl oxalate, and 2 grams finely pulverized sodium ethylate, together with 100 cc. anhydrous ether, were placed in a well-stoppered flask and left at the laboratory temperature for three weeks, with occasional shaking. No condensation occurred, the quinazolone being recovered unchanged.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY,
No. 203.]

RESEARCHES ON QUINAZOLINES (THIRTIETH PAPER). A STUDY OF THE BROMINATION AND NITRATION OF 4-QUINAZOLONES; THE CORRESPONDING AMINOQUINAZOLONES, AND CERTAIN OTHER NEW 4-QUINAZOLONES.¹

BY MARSTON TAYLOR BOGERT AND GEORGE AUGUSTUS GEIGER.

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The 4-quinazolones (4-hydroxyquinazolines) are not easily brominated by the action of bromine in aqueous potassium bromide solution, in glacial acetic acid or in acetic anhydride solution. By employing the Juvalta² process, however, the halogen may be introduced. In this way, monobromo derivatives have been obtained of 4-quinazolone and of 2-methyl-4-quinazolone.

Nor are the quinazolones readily nitrated. Griess,³ in 1869, showed that benzoylene urea could be nitrated, but did not prove the position of the nitro group. In 1890, Dehoff⁴ nitrated 2-methyl and 2,3-dimethyl-4-quinazolone, and his products were subsequently shown to be the 6-nitro derivatives by the investigations of Thieme⁵ and of Bogert and Cook.⁶

According to our experience, the satisfactory nitration of 4-quinazolones requires a high temperature and the use of a mixture of fuming nitric and concentrated sulfuric acids, and but one nitro group can thus be introduced on the 4-quinazolone nucleus. Position 6 seems to be the point where the nitro group enters most readily. Of course, aryl

¹ Read at the Washington Meeting of the Society, Dec. 29, 1911.

² D. R. P. 50,177, *Friedländer*, 2, 93.

³ *Ber.*, 2, 416 (1869).

⁴ *J. prakt. Chem.*, [2] 42, 347 (1890).

⁵ Thieme, *Ibid.*, 43, 473 (1891).

⁶ THIS JOURNAL, 28, 1449 (1906).

radicals attached to the quinazoline nucleus, at positions 2 or 3, for example, may also be nitrated in the reaction.

Nitration of the following gives mononitro derivatives: 4-quinazolone, 3-methyl-4-quinazolone, 3-ethyl-4-quinazolone and 2-methyl-3-ethyl-4-quinazolone. With 2-methyl-3-phenyl-4-quinazolone, a dinitro derivative results which is not identical with the dinitro compound obtained by nitrating 2-methyl-3-*p*-nitrophenyl-4-quinazolone. A dinitro derivative is also obtained from 2-methyl-3-*p*-tolyl-4-quinazolone.

The action of nitric acid upon 2-methyl-4-quinazolone, in presence of metallic mercury, gives only the mercury salt of the quinazolone, whereas with benzene dinitrophenol results, and with quinoline both an hydroxyl and nitro group are simultaneously introduced on the benzene portion of the molecule.¹

Griess² showed that nitro benzoylene urea could be reduced to the amino compound. Bogert and Chambers³ have prepared 5-amino-4-quinazolone, and Bogert and Klaber⁴ 7-amino-4-quinazolone, by reduction of the corresponding nitro compounds. Zacharias⁵ reduced 8-nitro-2-methyl-4-quinazolone, but failed to get a pure product. Dehoff² also failed in his attempt to reduce the 6-nitro-2-methyl-4-quinazolone.

Although the yields were generally poor, we have experienced no particular difficulty in reducing the 6-nitro-4-quinazolones to the corresponding amines, including the 6-nitro-2-methyl-4-quinazolone.

The new amino derivatives so prepared are as follows: amino and acetamino 4-quinazolone, amino and acetamino 3-methyl-4-quinazolone, 6-amino-2,3-dimethyl-4-quinazolone and 6-amino-2-methyl-3-ethyl-4-quinazolone.

In the prosecution of the research, the following new 4-quinazolones were also prepared: 3-ethyl, 3-benzyl-2-methyl-3-*p*-nitrophenyl, 2-methyl-3-*p*-tolyl, 2-methyl-3- α -naphthyl and 2-methyl-3- β -naphthyl.

Incidentally, it was found that the melting point of 71° assigned by Knape⁶ to 3-methyl-4-quinazolone is really that of the hydrated form, the anhydrous compound melting at 105° (cor.).

Experimental.

I. Simple 4-Quinazolones.

3-Methyl-4-quinazolone, $\text{HC} : \text{N.C}_6\text{H}_4.\text{CO.N.CH}_3$, was prepared first by Knape,⁸ by direct methylation of 4-quinazolone with potassium hydroxide and methyl iodide in methyl alcohol solution. The author states that

¹ Wolfenstein and Boeters, D. R. P. 214,045.

² *Loc. cit.*

³ THIS JOURNAL, 28, 207 (1906).

⁴ *Ibid.*, 30, 807 (1908).

⁵ *J. prakt. Chem.*, [2] 43, 443 (1891).

⁶ *Ibid.*, [2] 43, 216 (1891).

the crude product, washed with methyl alcohol and recrystallized from chloroform or ligroin, gave long needles of satiny luster, melting at 71° .

On repeating this process, and crystallizing the crude product from chloroform, we obtained colorless crystals, melting at 105° (cor.). This proved to be the pure anhydrous compound. When this quinazolone is crystallized from water, it carries a molecule of water of crystallization, and then melts at 71° , the point given by Knape.

The most convenient method of preparing the substance is to dissolve the 4-quinazolone in methyl alcohol containing the calculated amount of potassium hydroxide, add the required amount of methyl iodide, and let the mixture stand at laboratory temperature. In one and a half to two hours the solution changes to a mass of colorless crystals, which are filtered out and dissolved in the minimum amount of cold water. In about 15 minutes, the crystals separate again, and are then recrystallized from hot water, giving colorless needles, melting at $70-1^{\circ}$ (cor.).

These were dried in vacuum over concentrated sulfuric acid for four days, then heated at 80° for an hour, and again dried in vacuum for an hour:

Calculated for $C_9H_8ON_2 \cdot H_2O$: H_2O , 10.1. Found: H_2O , 10.0.

The dehydrated substance then melted at 105° (cor.). It was analyzed with the following result:

Calculated for $C_9H_8ON_2$: N, 17.50. Found: N, 17.32.

2,3-Dimethyl-4-quinazolone¹ also crystallizes from water with a molecule of water of crystallization, and it is interesting that the melting points of its hydrated and anhydrous forms are almost identical with those of the above 3-methyl compound:

3-Methyl, m. p. of hydrated form $70-1^{\circ}$; anhydrous m. p. 105° .

2,3-Dimethyl, m. p. of hydrated form 70° ; anhydrous m. p. $107-9^{\circ}$.

A mixture of the anhydrous forms of the two substances melts at $78-9^{\circ}$.

3-Ethyl-4-quinazolone.—20 grams 4-quinazolone were placed in a flask, sufficient ethyl alcohol added to make a thick paste, and then 7.6 g. solid potassium hydroxide. The flask was shaken until all the quinazolone had dissolved, 21 g. ethyl iodide poured in, and the mixture boiled under a return condenser until it showed a neutral reaction (about three-quarters of an hour). The alcohol was then distilled off, leaving a mass of potassium iodide crystals and a viscous liquid. This residue dissolved completely in 100 cc. cold water. As a previous experiment had shown that nothing could be separated from this aqueous solution by distillation with steam, it was extracted repeatedly with ether, adding some salt to the aqueous solution after the first extraction. The ether extracts were combined, dried with potassium carbonate (calcium chloride gives a yellower product), and the ether driven off, leaving the quinazolone as

¹ Weddige, *J. prakt. Chem.*, [2] 36, 147 (1887).

a crystallin mass. By careful recrystallization from ether, it was obtained in colorless needles, melting at 102° (cor.). Yield, 54% (13 g.). It may also be purified by distillation under reduced pressure (b. p. at 15 mm., 182°), when it comes over as a colorless oil, solidifying on cooling.

The pure compound dissolves also in water, alcohol, acetone or benzene, but does not crystallize well from any of these solvents.

Calculated for $C_{10}H_{10}ON_2$: N, 16.09. Found: N, 16.06.

3-Benzyl-4-quinazolone was prepared in similar manner from 4-quinazolone, methyl alcohol, potassium hydroxide and benzyl chloride. The reaction product was filtered hot from potassium chloride, and the desired quinazolone crystallized from the filtrate in colorless needles, which were washed with boiling water and recrystallized from dilute methyl alcohol, giving long, glassy needles, melting at 116° (cor.). Yield, 6 g. from 10 g. of quinazolone.

Calculated for $C_{15}H_{12}ON_2$: C, 76.27; H, 5.08; N, 11.86. Found: C, 76.08; H, 4.82; N, 11.98.

It is difficultly soluble in chloroform, benzene, acetone or alcohol, when cold, but dissolves in these solvents at their boiling points. It is but slightly soluble in ether.

2-Methyl-3-p-nitrophenyl-4-quinazolone, $CH_3.C : N.C_6H_4.CO.N.C_6H_4.NO_2$.—An intimate mixture of 4 g. acetanthranil and 3 g. *p*-nitraniline was heated for three-quarters of an hour at 190° . The gummy melt solidified on cooling. On repeated crystallization of this mass from alcohol, glistening, pale yellowish scales were obtained, melting at 193° (cor.). Yield, 2 g.

Calculated for $C_{18}H_{11}O_2N_3$: C, 64.05; H, 3.91; N, 14.94. Found: C, 63.81; H, 4.00; N, 15.04.

When *m*-nitraniline was used instead of the para compound, the desired quinazolone was not obtained.

2-Methyl-3-p-tolyl-4-quinazolone.—An intimate mixture of 10 g. acetanthranil and 7 g. *p*-toluidine was carefully heated. At about 80° , the mass began to melt, and at 100° steam was evolved. The temperature of the bath was slowly raised to 135° and kept there for half an hour. The melt was crystallized from dilute alcohol until pure, when it appeared in small, glistening, pale yellow scales, melting at 151° (cor.); soluble in benzene, acetone, chloroform or methyl alcohol, less readily in ether. Yield, 10 g.; or about 66% of theory.

Calculated for $C_{18}H_{14}ON_2$: N, 11.20. Found: N, 11.37.

2-Methyl-3- α -naphthyl-4-quinazolone.—An intimate mixture of acetanthranil and α -naphthylamine was heated gradually to 150° , and the temperature held at that point for about an hour. The resultant melt was poured while warm into excess of alcohol, the alcoholic solution pre-

precipitated by careful dilution with water, and the precipitate recrystallized from dilute alcohol. Small, nearly colorless plates were obtained, melting at 136° (cor.), which possessed an odor resembling that of α -naphthylamine, possibly due to a trace of this substance, and which turned a pale pink on standing in the air. Yield, 10.5 g. The compound is soluble in acetone, chloroform or benzene, and less easily in ether.

Calculated for $C_{19}H_{14}ON_2$: N, 9.79. Found: N, 9.82.

2-Methyl-3- β -naphthyl-4-quinazolone, prepared in practically the same way, crystallizes from alcohol in nodules of short needles, of a pinkish cast, melting at 175° (cor.), and is less soluble in alcohol than the α -compound.

Calculated for $C_{19}H_{14}ON_2$: N, 9.79. Found: N, 9.91.

II. Bromination of 4-Quinazolones.

Monobromo - 4 - quinazolone, $\text{HC} : \text{N.C}_6\text{H}_3\text{Br.CO.NH.}$ —Attempts to brominate 4-quinazolone with a solution of bromine in aqueous potassium bromide, or by bromine in acetic acid solution, all failed. The Juvalta¹ process was therefore applied.

Two grams of the quinazolone were dissolved in 60 cc. fuming sulfuric acid and 2 cc. bromine gradually added. The temperature was raised slowly to 115° and kept there for an hour and a half. When cold, the solution was partly neutralized with solid sodium carbonate and then poured into about 300 cc. ice water. A brownish precipitate separated. It was filtered out, dissolved in dilute alcohol, the hot solution decolorized with bone-black and filtered. From the filtrate, on cooling, there separated a colorless flocculent mass, which was further purified by dissolving it in dilute potassium hydroxide solution and reprecipitating with acetic acid.

Calculated for $C_8H_5ON_2\text{Br}$: N, 12.44; Br, 35.55. Found: N, 12.28; Br, 35.79.

The compound melts at 258° (uncor.). It is soluble in acetone, methyl or ethyl alcohols; insoluble or difficultly soluble in water, benzene, ether or chloroform.

Monobromo-2-methyl-4-quinazolone, $\text{CH}_3\text{C} : \text{N.C}_6\text{H}_3\text{Br.CO.NH.}$ —Addition of bromine to the quinazolone in glacial acetic acid or acetic anhydride solution yielded what was apparently only the hydrobromide of the original substance, since on dissolving it in dilute potassium hydroxide solution and reprecipitating with carbon dioxide, the quinazolone was recovered. Similar results were recorded when the quinazolone was triturated in a mortar to a thick paste with a solution of bromine in aqueous potassium bromide and the paste then dried at 110° .

In this case also, it was necessary finally to resort to the Juvalta method,

¹ *Loc. cit.*

as described for the 4-quinazolone itself, the reaction being carried out in a similar manner. The product obtained by dissolving the crude substance in dilute potassium hydroxide solution and precipitating with acetic acid was colorless and gelatinous. Dried at 110° , it melted at 277° (uncor.). Yield, 55%.

Calculated for $C_8H_7ON_2Br$: N, 11.71; Br, 33.47. Found: N, 11.73; Br, 33.99.

It is moderately soluble in cold methyl alcohol, soluble in hot acetone, insoluble in ether or benzene.

III. Nitration of 4-Quinazolones.

Mononitro-4-quinazolone, $\text{HC} : \text{N.C}_6\text{H}_4(\text{NO}_2).\text{CO.NH.}$ —Fuming nitric acid (sp. gr. 1.6) alone failed to nitrate the quinazolone.

Five grams of the quinazolone were added carefully to a mixture of 10 cc. concentrated sulfuric and 10 cc. fuming (sp. gr. 1.6) nitric acids, the solution concentrated to half its volume, cooled, and poured into 500 cc. ice water. The nitro derivative separated in beautiful, silky, yellow plates. Washed with water, the compound lost its crystalline character and became granular and pulverulent. It was further purified by solution in sodium hydroxide and reprecipitation with acetic acid. As thus purified, it forms a practically colorless powder, darkening slightly at about 275° , and melting with decomposition at 284° (uncor.). Yield, 60%.

Calculated for $C_8H_5O_2N_3$: N, 21.99. Found: N, 21.63, 22.15.

It is moderately soluble in hot water, and in methyl or ethyl alcohol; insoluble or difficultly soluble in benzene, ether or chloroform. It dissolves in dilute sodium hydroxide solution to a yellow or reddish solution depending upon the concentration. With sodium hydroxide and methyl iodide, it gives the 3-methyl derivative. Its nitro group is very probably at position 6.

6-Nitro-2-methyl-4-quinazolone, $\text{CH}_3.\text{C} : \text{N.C}_6\text{H}_4(\text{NO}_2).\text{CO.NH.}$ —Five grams of the quinazolone were added gradually to 25 cc. fuming nitric acid (sp. gr. 1.52) and the solution then concentrated to half its volume. When cold, the solution was poured into 50 cc. ice water, and the precipitated nitro-quinazolone purified by crystallization from dilute alcohol, or by dissolving in dilute sodium hydroxide solution and reprecipitating with carbon dioxide or acetic acid.¹ Yield, 66%. The pure substance forms pale yellow needles which begin to decompose at about 266° and melt at 299° (uncor.). Small amounts of impurities depress this melting point considerably, and the figure $278-81^{\circ}$ given by Bogert and Cook² was obtained on an insufficiently purified sample, as we have proven by

¹ Dehoff, *Loc. cit.*

² *Loc. cit.*

examining their original material, further purification of which raised its melting point to 299° .

When this compound is heated with concentrated hydrochloric acid in a sealed tube at 250° , decomposition and charring result.

The influence of the presence of metallic mercury in the above nitration was also investigated. The interaction of the quinazolone, fuming nitric acid (sp. gr. 1.4 or 1.5) and metallic mercury, irrespective of the order in which they were mixed, invariably yielded a dark mass which when poured into cold water gave a yellow to brownish precipitate, insoluble in dilute aqueous caustic alkalis, alcoholic alkali, benzene, nitrobenzene, aniline, ether, chloroform, toluene, amyl alcohol or amyl acetate; but soluble in hot, glacial acetic acid or in mineral acids. Neutralization of the acetic acid solution by sodium hydroxide yielded a yellow gelatinous precipitate, which crystallized from glacial acetic acid as a yellow powder, melting above 360° , and proved to be the mercury salt of the original unnitrated quinazolone:

Calculated for $C_8H_7ON_2Hg$: N, 7.79. Found: N, 7.85. The presence of mercury in the compound was demonstrated qualitatively.

Mononitro-3-methyl-4-quinazolone, $\overline{HC : N.C_6H_3(NO_2).CO.N.CH_3.}$ — A mixture of 5 g. nitro-4-quinazolone and 125 cc. methyl alcohol, with the calculated amounts of potassium hydroxide and methyl iodide, was boiled gently for two hours under a reflux condenser. On cooling, the methyl derivative crystallized out. Recrystallized from methyl alcohol, it was obtained in colorless crystals, melting at 196° (cor.).

The same substance was obtained by nitrating 5 g. of anhydrous 3-methyl-4-quinazolone with 20 cc. of a mixture consisting of one-third concentrated sulfuric and two-thirds fuming nitric (sp. gr. 1.6) acids, evaporating to one-third the original volume, cooling, pouring upon ice, and recrystallizing the crude product from water. Yield, about 70%. When pure, the substance is nearly colorless. It is soluble in water, alcohol, acetone or benzene, but not appreciably soluble in ether.

Calculated for $C_9H_7O_3N_3$: N, 20.48. Found: N, 20.64.

Mononitro-3-ethyl-4-quinazolone, $\overline{HC : N.C_6H_3(NO_2).CO.N.C_2H_5.}$ — Two grams of 3-ethyl-4-quinazolone were added to a mixture of 5 cc. concentrated sulfuric and 15 cc. fuming (sp. gr. 1.52) nitric acids and the whole boiled down to about half its volume, cooled, and poured upon ice. Fine, colorless needles separated which became pulverulent when washed with water. Recrystallized from water, it was obtained in colorless, thin needles, melting at 165° (cor.). Yield, 1.2 g. (47%). It is also soluble in alcohol. The nitro group is most probably at position 6.

Calculated for $C_{10}H_9O_3N_3$: N, 19.18. Found: N, 19.33.

6-Nitro-2-methyl-3-ethyl-4-quinazolone, $\text{CH}_3\text{C}:\text{N}.\text{C}_6\text{H}_3(\text{NO}_2).\text{CO}.\text{N}.\text{C}_2\text{H}_5$. — Five grams of the methylethylquinazolone were added to a mixture of 15 cc. concentrated sulfuric and 20 cc. fuming (sp. gr. 1.52) nitric acids, and the nitric acid boiled off. The cold acid solution was poured upon cracked ice, and the nitro derivative separated in short, fine needles which crumbled to a powder when thoroughly washed with water and dried. Yield, 80%. The compound showed the same melting point 166° (cor.) as recorded for this substance by Bogert and Cook,¹ who prepared it from the corresponding nitroanthranilic acid.

Dinitro-2-methyl-3-phenyl-4-quinazolone. — The methylphenylquinazolone was nitrated by a mixture of one part concentrated sulfuric to two parts fuming (sp. gr. 1.52) nitric acid, the solution concentrated, cooled, and poured upon cracked ice. The nitrated product separated in very fine, yellowish needles, not appreciably soluble in water, methyl or ethyl alcohols, ether, chloroform or benzene. From acetone, or from glacial acetic acid, it separates in microscopic crystals of faint yellowish cast, melting at 267° (uncor.). Yield, 65%.

Calculated for $\text{C}_{15}\text{H}_{10}\text{O}_5\text{N}_4$: N, 17.17. Found: N, 17.21.

The compound is evidently a dinitro derivative, and it was suspected that one nitro group had entered position 6, as usual, and that the other had probably attached itself to the 3-phenyl group, most likely in the para position, as is the case in nitrating 2-styryl-4-quinazolone.² Nitration of 2-methyl-3-*p*-nitrophenyl-4-quinazolone, as recorded beyond, did not give the same substance, and this part of the investigation was not carried further on account of the withdrawal of the junior author to take up other work. In our opinion, the compound is most probably the 6-nitro-2-methyl-3-*o*-nitrophenyl-4-quinazolone, since 2-methyl-3-*p*-tolyl-4-quinazolone also yields a dinitro derivative.

*Nitro-2-methyl-3-*p*-nitrophenyl-4-quinazolone*. — The nitration was carried out in a manner similar to that used in the previous cases, and showed that only one more nitro group could be introduced under these conditions. The position probably taken by the entering nitro group is at 6, as already explained. The product crystallized from glacial acetic acid in clusters of small, golden yellow scales, melting with decomposition at 264° (uncor.), and insoluble in water or alcohol.

Calculated for $\text{C}_{15}\text{H}_{10}\text{O}_5\text{N}_4$: N, 17.17. Found: N, 17.34.

A mixture of this with the foregoing dinitro body showed a melting point of 225° (uncor.).

*Dinitro-2-methyl-3-*p*-tolyl-4-quinazolone*. — The nitration of 2-methyl-3-*p*-tolyl-4-quinazolone in the same way also resulted in the production

¹ *Loc. cit.*

² Bogert and Beal, *THIS JOURNAL*, 34, 516 (1912).

of a dinitro derivative, insoluble in water or alcohol, but dissolving in glacial acetic acid. On diluting the latter solution, it separated in minute, pale yellow crystals, shriveling at 262° and melting with decomposition at 275° (uncor.). Yield, 1.2 g. quinazolone. We think it likely that one of the nitro groups in this compound is at position 6, and the other one in the *p*-tolyl nucleus.

Calculated for $C_{16}H_{11}O_2N_4$: N, 16.47. Found: N, 16.75.

IV. Reduction of the Nitro to the Corresponding Amino 4-Quinazolones.

Amino-4-quinazolone, $HC : N.C_6H_4(NH_2).CO.NH$. — The nitro compound was reduced with stannous chloride and hydrochloric acid, and the tin removed by hydrogen sulfide. After the elimination of the tin, the solution was made alkaline with potassium hydroxide, filtered, and the filtrate neutralized exactly. Feathery masses of short, fine needles separated. Recrystallized from water, these needles melted at 318° (cor.). Yield, about 20%. The substance is soluble in dilute acids or in alkalies.

Calculated for $C_8H_7ON_3$: N, 26.08. Found: N, 25.95.

Acetamino-4-quinazolone, from the aminoquinazolone and acetic anhydride, crystallizes from water in colorless, short, silky needles, melting at 335° (cor.). Yield, 90%.

Calculated for $C_{10}H_9O_2N_3$: N, 20.69. Found: N, 20.57.

6-Amino-2-methyl-4-quinazolone. — The nitroquinazolone was reduced with stannous chloride (or tin) and hydrochloric acid, and the reduction product separated as described for the amino-4-quinazolone. The yield was fair and the product, after recrystallization from water, melted at $314-5^{\circ}$ (cor.), with preliminary softening at about 304° . It forms long, colorless, silky needles, soluble in dilute acids or alkalies. This product was found to be identical with the 6-amino-2-methyl-4-quinazolone prepared by Bogert, Amend and Chambers¹ from 2,5-diacetaminobenzoic acid. Both products showed the same melting point, and when the two were intimately mixed the melting point of the mixture was the same.

Dehoff² tried the above reduction of the nitroquinazolone but, apparently through lack of sufficient initial material, failed to get the amino compound.

Calculated for $C_9H_9ON_3$: N, 24.00. Found: N, 24.12.

6-Acetamino-2-methyl-4-quinazolone was obtained from the aminoquinazolone by the action of acetic anhydride and purified by crystallization from water. It forms fine, colorless needles which, when heated, turn brownish at about 335° and melt at 351° (cor.). Bogert, Amend

¹ THIS JOURNAL, 32, 1311 (1910).

² *Lec. cit.*

and Chambers prepared the same substance from 5-acetaminoacetan-
thranil and ammonia, and found its melting point to be 350° (cor.). A
mixture of the two products showed a melting point of 349° (cor.), and
in either respect they were found to be identical. When the 7-acetamino
isomer (m. p. 344° , cor.) was mixed with this product, the melting point
of the mixture dropped to 311° (cor.).

Amino-3-methyl-4-quinazolone, $\text{HC} : \text{N.C}_6\text{H}_3(\text{NH}_2).\text{CO.NCH}_3$.—The cor-
responding nitro compound was reduced with stannous chloride and
hydrochloric acid, warming to complete the reaction. On cooling, color-
less crystals separated. These were dissolved by adding three volumes
of hot water, and the tin precipitated by hydrogen sulfide. The filtrate
from the tin sulfide was boiled to remove hydrogen sulfide, then made
alkalin, filtered hot, and on cooling the amine separated from the filtrate
in small, colorless needles. Recrystallized from water, the substance
melts at 209° (uncor.). Yield, 20%.

Calculated for $\text{C}_9\text{H}_9\text{ON}_2$: N, 24.00. Found: N, 23.96.

Acetamino-3-methyl-4-quinazolone, prepared from the above by the
action of acetic anhydride, crystallizes from water in thin, colorless, silky
needles, melting at 269° (uncor.).

Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2$: N, 19.35. Found: N, 19.47.

6-Amino-2,3-dimethyl-4-quinazolone.—The corresponding nitroquinazo-
lone was reduced with stannous chloride and hydrochloric acid, detinning
with hydrogen sulfide, boiling out excess of the latter, filtering, making
the filtrate alkalin and filtering hot. From this hot, alkalin filtrate,
the amine separated on cooling and was recrystallized from water. It
forms colorless, thin, silky needles, melting at 244° (uncor.). Yield, 10%.

Calculated for $\text{C}_{10}\text{H}_{11}\text{ON}_2$: N, 22.22. Found: N, 22.33.

6-Amino-2-methyl-3-ethyl-4-quinazolone was prepared in a similar man-
ner from the nitro compound by reduction with stannous chloride and
hydrochloric acid. It crystallizes from water in long, thin, colorless
needles, melting at 185° (cor.). Yield, 20%.

Calculated for $\text{C}_{11}\text{H}_{13}\text{ON}_2$: N, 20.69. Found: N, 20.63.

V. Other Experiments with 2-Methyl-4-quinazolone.

The stability of this substance towards hot, concentrated hydrochloric
acid under pressure was tested with the following results, using 5 cc. of
the acid per gram of quinazolone:¹

1. Six hours at 155° . No apparent change.
2. Six hours at 190° . Slight decomposition and some pressure in the
tube. From 2 g. quinazolone, 1.8 g. of the hydrochloride were recovered.
3. Six hours at 216° . Partial decomposition, with considerable pres-
sure in the tube. From 2 g. quinazolone, about 1.5 g. of the hydrochloride

¹ Compare Bogert and Seil, THIS JOURNAL, 28, 890 (1906).

were recovered, and a small amount of what appeared to be aniline hydrochloride.

4. Six hours at 250°. Complete decomposition of the quinazolone into aniline, ammonia and carbon dioxide. Crystals of ammonium chloride separated in the tube.

2-Methyl-4-quinazolone and Benzoyl Chloride.—Ellinger and Riesser¹ found that, by the action of benzoyl chloride upon 4-hydroxyquinoline, 4-chlorquinoline could be obtained. It therefore seemed worth trying this reagent upon 2-methyl-4-hydroxyquinazoline (2-methyl-4-quinazolone), in the hope that here too the hydroxyl group might be replaced by chlorine, since all other methods so far used to get this chlorquinazoline have failed. Experiments directed to this end, however, proved unsuccessful. When a mixture of five grams of the quinazolone and 50 cc. benzoyl chloride were heated together, the quinazolone slowly dissolved, and in three hours a clear solution was obtained, but no chlorquinazoline could be recovered from the dark liquid.

NEW YORK CITY.

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STUDIES ON MALIC ACID. I. THE TRANSFORMATION OF MALIC ACID TO SUGAR BY THE TISSUES OF THE MAPLE (ACER SACCHARINUM).

BY W. R. BLOOR.

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Although malic acid is one of the most widely distributed plant acids, very little is known definitely of its chemical relations to the other organic plant substances, or of its function in the plant organism. Together with tartaric and citric acids, malic acid is generally regarded as a product of "intramolecular" respiration and, like them, is most closely related to glucose. In certain members of the Crassulaceae—thick-leaved desert plants which have adapted themselves to life in places where moisture and carbon dioxide are scarce—it has been demonstrated by Kraus² that there is an accumulation of malic acid at the expense of the sugar during the night, and a transformation of malic acid into sugar during the day. By this process of molecular rearrangement the plant is supplied with energy during the night while the precious carbon dioxide is preserved for use during the succeeding day. These same plants use malic acid also as a form of reserve material, the calcium malate deposited often amounting to half the dry weight of the leaf. The disappearance of malic acid accompanied by an increase of sugar is well known

¹ Ber., 42, 3336 (1909).

² Kraus, Abhandl. Naturforsch. Gesellsch. Halle, 16, 393 (1886).

to take place during the ripening of fruits which contain malic acid, *e. g.*, the apple. In neither case is the transformation quantitative, considerably more malic acid disappearing than can be accounted for by the sugar formed. It became of interest to know whether the ability to transform malic acid to sugar is common to all plants which produce malic acid.

Maple sap contains malic acid in the form of neutral calcium malate to the extent of about 1% of the sugar content, and since a supply of this material—the so-called “sugar sand”—became available¹ it was decided to determine whether the tissues of the maple could effect the above transformation. Presumably the power to bring about the change would be most marked in those parts of the tree which were showing signs of life at the time of the sap flow—the swelling buds and the shoots which carried them—and these tissues were accordingly used for the experiment.

The malic acid preparations used were:

1. Neutral calcium malate obtained by twice recrystallizing the “sugar sand.”
2. Acid calcium malate, obtained by precipitating half the calcium from the neutral malate by means of oxalic acid, and recrystallizing the product.
3. Malic acid—by removal of all the calcium from the crude neutral malate by oxalic acid. This product contained a small amount of cane sugar as impurity.
4. Pure malic acid—by precipitation of all the calcium from the calcium malate of preparation 1.

Well developed, healthy shoots of *Acer Saccharinum*, of the previous year's growth, were collected at the time when the leaf buds first showed signs of swelling and later when the buds had opened and before much growth had taken place. The buds were separated from the shoots and both treated as follows: After a preliminary washing with cold water, the tissues were chopped as fine as possible, ground in a meat mill till well disintegrated, and used at once for the experiments, which were carried out as follows.

Five to six grams of the fresh tissue were weighed into a 350 cc. Erlenmeyer flask, 200 cc. of boiled water added and then enough of the malic acid preparation to make a 0.5% solution was measured in with a pipet. Ten cubic centimeters of xylene were added as a preservative, the mixture well shaken, loosely stoppered and placed in a south window. A mixture containing all the substances except the malic acid was similarly treated and used as a blank. After exposing to sunlight for a suitable time, the acidity and the sugar content of each solution were determined in the following way:

¹ Through the kindness of Dr. W. H. Warren, formerly of this school.

Acidity.—Determined by titration with standard alkali and phenolphthalein. Correction was made for initial acidity (due to the malic acid preparation) and for the acidity of the blank.

Sugar.—To the neutral mixture from above was added 15 cc. of 10% neutral lead acetate, the solution shaken, filtered, and the precipitated lead malate washed twice with cold water. To the filtrate was added excess of sulfuric acid, the precipitated lead sulfate filtered off and the filtrate and washings boiled to hydrolyze any disaccharides present. After neutralization with sodium hydroxide and filtering, sugar was determined by Allihn's method. Correction was made for reducing substance in the blank and when necessary, in the malic acid preparations.

MAPLE SHOOTS.

SERIES I.—SUNLIGHT.

0.5% solutions of neutral calcium malate, acid calcium malate, and malic acid.

	Change in acidity, cc. 0.1 N.	Change in reduction, Mg. Cu ₂ O.
Experiment I.—2 days' sunlight.		
Neutral Ca malate.....	Loss, 0.7	No change
Acid Ca malate.....	Loss, 2.1	Gain, 47.0
Malic acid.....	Loss, 9.7	Gain, 131.2

Experiment II.—4½ days' sunlight.

Neutral Ca malate.....	No change	Gain, 34.0
Acid Ca malate.....	Loss, 8.4	Gain, 136.2
Malic acid.....	Loss, 18.2	Gain, 92.0

Experiment III.—2 days' sunlight, 1 dull day.

Acid Ca malate.....	Loss, 0.75	Loss, 8.0
Pure malic acid.....	Loss, 7.5	Loss, 16.0
Malic acid (containing sugar, prep. 3).....	Loss, 5.25	Gain, 4.6
Pure malic acid (1% solution).....	Loss, 17.3	Gain, 16.0
Malic acid (1% solution).....	Loss, 1.5	Gain, 14.0

Experiment IV.—10 days' sunlight, 2 dull days.

Acid Ca malate.....	Loss, 3.0	Gain, 54.0
Pure malic acid.....	Loss, 14.3	Gain, 42.0
Malic acid (containing sugar).....	Loss, 11.2	Gain, 61.0
Pure malic acid (1% solution).....	Loss, 5.8	Gain, 82.0
Malic acid (1% solution).....	Loss, 22.3	Gain, 99.0

The tissue of maple shoots in solutions of malic acid or malates is here shown to produce, in nearly all cases, an increase in the reducing power together with a decrease in the acidity of the solutions. There is no constant relation between the loss of acidity and the gain in reducing power.

MAPLE SHOOTS.

Series II. Incubator.

In order to determine whether light was necessary for the transformation, some experiments were carried on in an incubator at a temperature of 38°. The solutions as before contained 0.5% of the malic acid compound.

	Change in acidity, cc. 0.1 N.	Change in reduction, Mg. Cu ₂ O.
Experiment I.—3 days.		
Acid Ca malate.....	Loss, 4.47	Gain, 7.0
Pure malic acid.....	Loss, 5.7	Loss, 33.0
Malic acid (with sugar).....	Loss, 5.7	Gain, 8.0
Experiment II.—4 days.		
Acid Ca malate.....	Loss, 1.49	Gain, 24.0
Pure malic acid.....	Loss, 6.50	Gain, 63.2
Malic acid (with sugar).....	No change	Loss, 5.0
Experiment III.—8 days.		
Acid Ca malate.....	Loss, 2.8	Gain, 7.7
Malic acid (with sugar).....	Loss, 8.94	Loss, 35.7

In this series there is a lack of constancy of results, which is probably due to the much more favorable conditions for bacterial growth. The net results, however, indicate that the changes noted in Series I may be produced by warmth alone and that therefore light is not necessary for the transformation. There is then a strong probability of enzyme action.

MAPLE SHOOTS.

Series III. Tissue boiled for five minutes.

These experiments were made to determine whether the changes noted were caused by enzymes; also to exclude the possibility of an increase in reducing power due to hydrolysis of sugar-producing substances in the tissue by the malic acid. The solutions containing the maple tissue were boiled for five minutes.

	Change in acidity, cc. 0.1 N.	Change in reduction, Mg. Cu ₂ O.
Experiment I.—3 days' sunlight.		
Acid Ca malate.....	Loss, 1.5	Slight gain
Pure malic acid.....	Loss, 7.5	Gain, 7.6
Malic acid (with sugar).....	Loss, 7.5	Gain, 4.1
Experiment II.—6 days (4 cloudy, 2 sunlight).		
Acid Ca malate.....	Loss, 2.2	Loss, 17.0
Pure malic acid.....	Loss, 12.6	Loss, 5.5
Malic acid (containing sugar).....	Loss, 7.5	Gain, 11.0
Experiment III.—13 days (10 sunlight).		
Acid Ca malate.....	Gain, 1.5	Gain, 4.0
Pure malic acid.....	Loss, 3.0	No change
Malic acid (with sugar).....	Gain, 1.1	Loss, 20.7

Boiling prevents any appreciable increase in reducing power, indicating the probable presence of an enzyme in the tissues, and excluding the

possibility of hydrolysis due to the acidity of the solutions. An attempt was made to extract the enzyme with water. About 9 g. of the finely divided shoots were allowed to stand in water over night, the extract filtered off, mixed with the malic acid preparations and diluted with water to the same volume as before.

MAPLE SHOOTS.

Series IV. Water Extract.

	Change in acidity, cc. 0.1 N.	Change in reduction, mg. Cu ₂ O.
Experiment I.—4 sunny, 2 cloudy days.		
Acid Ca malate.....	Gain, 1.52	Gain, 7.8
Malic acid, pure.....	Gain, 5.2	Gain, 15.2
Malic acid, impure (containing sugar).....	No change	Gain, 42.6
Experiment II.—4½ days' bright sunshine.		
Acid Ca malate.....	Loss, 2.22	No change
Malic acid, pure.....	Loss, 4.44	Gain, 20.0
Malic acid (containing sugar).....	No change	Loss, 25.0

The results indicate that the active principle is somewhat soluble in water.

MAPLE BUDS (LEAF BUDS).

0.5% solutions of neutral calcium malate, acid calcium malate, and malic acid.

	Change in acidity, cc. 0.1 N.	Change in reduction, mg. Cu ₂ O.
Experiment I.—Buds swelling. 2 days' sunlight.		
Neutral Ca malate.....	Gain, 6.25	Loss, 48.0
Acid Ca malate.....	No change	Loss, 29.0
Malic acid (containing sugar).....	Loss, 11.9	Loss, 40.0
Experiment II.—Buds swelling. 4½ days' sunlight.		
Neutral Ca malate.....	No change	No change
Acid Ca malate.....	Loss, 2.23	No change
Malic acid (containing sugar).....	Loss, 11.9	Loss, 37.0
Experiment III.—Buds opening. 2 days' sunlight.		
Acid Ca malate.....	Gain, 15.6	Loss, 94.5
Malic acid.....	Gain, 52.5	Loss, 43.0
Experiment IV.—Buds opening. 10 days' sunlight.		
Acid Ca malate.....	Gain, 15.6
Malic acid.....	Gain, 47.6	Loss, 39.4

The tissues of the swelling buds mixed with solutions of malic acid or its salts cause a decrease in the reducing power of the solutions, which is generally accompanied by an increase of acidity. The change is more marked in the more rapidly growing (opening) buds and probably means a breaking down of the sugar by the growing tissues.

The experiments reported above were carried out in the spring of 1911 and were limited to the time of opening of the leaf buds. For obvious reasons the work is incomplete, but as circumstances prevent its con-

tinuance for some time, the foregoing results are offered with the expectation of supplementing them later as opportunity permits.

In conclusion, I wish to express my appreciation of the kindness of Prof. G. T. Moore, of the Missouri Botanical Gardens, in placing at my disposal the resources of the gardens.

Conclusions.

The tissue of maple shoots, when mixed with solutions of malic acid or malates and exposed to sunlight, cause an increase in reducing power and a decrease of acidity in the solutions—which may be interpreted to mean a transformation of the malic acid into sugar.

A less pronounced change of the same kind is produced in darkness at 38°.

The active principle which produces the change is somewhat soluble in water, is destroyed by boiling and is therefore probably of enzyme nature.

The tissue of maple buds similarly treated brings about a decrease of reducing substance and an increase of acidity in solutions of malic acid or its salts.

[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY, BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE.]

OSMOTIC ACTIVITY IN THE EGG OF THE COMMON FOWL.¹

BY A. D. GREENLEE.

Received January 26, 1912.

Introduction.

Eggs, when fresh, contain a large percentage of moisture, and like all other highly aqueous substances they lose moisture on standing by evaporation to the external atmosphere. Chemical analyses of eggs by various investigators are fairly numerous, but little has been done to correlate the change in moisture content with the age or condition of the egg. König² reports an analysis of eggs by Bostock as early as 1855. Langworthy³ determined the percentage in the whole egg with and without the shell, and on the white and yolk separate, and on boiled eggs. Lebbin⁴ found the relative percentage of yolk, white, and shell. Cook⁵ made a more extensive study of eggs, and, together with other changes, found that "eggs in storage for one year show a loss of weight equivalent to 10% of the total weight, which loss is largely water from the whites." He also found that "when fresh eggs are boiled a loss in weight

¹ Preliminary paper.

² *Chemie der Menschlichen Nahrungs und Genussmittel*, 1, 98.

³ U. S. Dept. Agr., *Farmers' Bulletin* 128.

⁴ *Z. öffent. Chemie*, 6, 148 (1900).

⁵ U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 115.

occurs, while storage eggs gain on boiling. Apparently the whites lose more water than do the yolks and consequently gain more when boiled. The boiled yolks when fresh contain less than 50% of water; when cold-stored this percentage is increased, the figure reaching 64% in the last examination."

Pennington¹ in a rather extensive study of fresh eggs determined the moisture on several samples for the whites and yolks separately and established averages which have served as the basis of many calculations in this work.

Moisture Determinations.

The White Leghorn eggs used for this investigation were obtained from a poultry farm and were not more than 24 hours old when the experiment began. They were kept in the ordinary commercial 30-dozen egg crate at a temperature of 32° F.; those held at higher temperatures were in pasteboard cartons, each holding 1 dozen. The cartons were so arranged that they were not in juxtaposition, in order to give a uniform exposure to the atmosphere. An analysis of the fresh eggs was made and then of other samples from the lots held at 32° F. at intervals of from one to three months and from the higher temperature lots at intervals of from three to ten days. Two dozen eggs were usually taken for a sample in order to insure uniformity. The results of the moisture determinations are recorded in Table I.

TABLE I.—PERCENTAGE CHANGE OF THE MOISTURE CONTENT OF WHITE AND YOLK ON HOLDING AT DIFFERENT TEMPERATURES FOR VARYING PERIODS.

Expt. 196 (32° F.).			Expt. 197 (32° F.).			Expt. 356 (32° F.).			Expt. 357 (32° F.).		
Age in days.	White.	Yolk.	Age in days.	White.	Yolk.	Age in days.	White.	Yolk.	Age in days.	White.	Yolk.
41	87.42	49.15	43	87.54	48.80	0	88.25	47.35	14	88.75	47.17
76	87.15	49.77	83	86.42	49.25	14	87.59	47.87	21	88.06	47.54
166	86.65	50.25	197	86.30	50.54	35	87.55	48.05	35	87.94	48.08
201	86.19	49.73	268	85.96	50.81	49	87.10	49.35	49	88.16	48.37
266	85.35	50.60
Expt. 363 (52° F.).			Expt. 355 (65° F.).			Expt. 334 (70° F.).			Expt. 336 (80° F.).		
Age in days.	White.	Yolk.	Age in days.	White.	Yolk.	Age in days.	White.	Yolk.	Age in days.	White.	Yolk.
0	88.24	46.63	0	87.66	47.64	0	87.60	47.17	0	87.75	47.97
14	87.57	47.80	7	86.71	48.96	6	87.09	48.53	7	86.98	49.00
35	87.44	49.39	18	86.11	50.28	13	86.63	49.13	11	86.51	49.72
..	34	85.99	50.56	19	86.45	49.26	15	86.77	49.78
..	26	85.16	50.27	19	85.89	50.44
..	33	85.09	50.19
..	40	84.74	50.60

Interpretation of Results.

The decrease in moisture in the white appears to be easily accounted for by evaporation to the external atmosphere, but the loss in weight

¹ *J. Biol. Chem.*, 7, 109 (1910).

as shown by means of the balance is not sufficient to account for the entire decrease in the percentage of moisture. This fact, together with the increased moisture in the yolk, suggests a transfer of water from white to yolk.

As far as the results given in Table I indicate, it can not be definitely proved that water passes from the white to the yolk. The same results would be obtained if the white took up solids from the yolk, and the yolk would apparently increase in water if, during the process of desiccation in the determination of solids in the oven at 100° C., some of the solids were volatilized. The two chief constituents in the yolk, aside from water, are fat and protein. A determination of the Reichert-Meissl number of the extracted fat indicates no increase of volatile fatty acids, from which it may reasonably be assumed that there is no volatilization of fatty substance. Furthermore, an analysis of the dried sample gives the same percentage of nitrogen as the percentage of nitrogen in the fresh sample calculated on the water-free basis, which would show that there is no loss of nitrogenous or protein matter. By a process of mathematical calculation it can easily be shown that solids have not passed from the yolk to the white. Although the yolk has decreased in the percentage of its solids by about the same number of points that the white has increased, nevertheless, since the percentage of solids in the yolk greatly exceeds that in the white, the amount which it would be necessary for the yolk to lose in order to account for the experimental data would be more than sufficient to raise the percentage of solids in the white to the experimental figures, regardless of the fact that there is almost twice as much white as yolk, and even if there were no loss of moisture to the external atmosphere.

This phenomenon of a transfer of water from the white to the yolk may easily be explained by the simple process of osmosis. The yolk, which contains a very high percentage of solids, is surrounded by a membranous tissue called the vitellin membrane, which in turn is surrounded by the egg white, a liquid much more dilute than the yolk. By osmosis the water passes through the membrane from the more dilute to the more concentrated solution until an equilibrium is obtained. In the egg this process continues until the vitellin membrane becomes so weak that it breaks, when the white and yolk begin to lose their identity. This action proceeds with such definiteness that by a process of calculation, knowing the original weight of the egg, the loss in moisture to the external atmosphere can be calculated with surprising closeness to the actual loss as shown by the balance. The following examples are given:

EXAMPLE I. No. 334 1-7 (40 days at room temperature).

(Fresh eggs = 59.35% white, 30.39% yolk, 10.26% shell.)

561 grams = original weight of 10 fresh eggs.

$561 \times 59.35\% = 323.95$ grams, original weight of white in 10 fresh eggs.
 $561 \times 30.39\% = 170.49$ grams, original weight of yolk in 10 fresh eggs.
 $323.95 \times 12.40\% = 41.28$ grams, solids in white of 10 eggs.
 $170.49 \times 52.83\% = 90.07$ grams, solids in yolk of 10 eggs.
 $41.28 \div 15.26\% = 270.52$ grams, final weight of white.
 $90.07 \div 49.40\% = 182.33$ grams, final weight of yolk.
62.43 grams = total loss to white (calculated).
11.84 grams = total gain to yolk (182.33-170.49).
50.59 grams = loss to external atmosphere (calculated).
(Experimental loss to 10 eggs as taken from No. 334-7 shows an average of 49.53 gram .)

EXAMPLE II. No. 336 1-5 (19 days at room temperature).

556.6 grams = original weight of 10 fresh eggs.
 $556.6 \times 59.35\% = 330.34$ grams, original weight of white in 10 eggs.
 $556.6 \times 30.39\% = 169.15$ grams, original weight of yolk in 10 eggs.
 $330.34 \times 12.25\% = 40.46$ grams, solids in white of 10 eggs.
 $169.15 \times 53.02\% = 88.01$ grams, solids in yolk of 10 eggs.
 $40.46 \div 14.11\% = 286.8$ grams, final weight of white.
 $88.01 \div 49.56\% = 177.6$ grams, final weight of yolk.
43.54 grams = total loss to white (calculated).
8.40 grams = total gain to yolk (calculated).
35.14 = loss to external atmosphere (calculated).
35.83 = average loss to 10 eggs as shown by experiment No. 336-5.

TABLE II.—PERCENTAGE OF SHELL, WHITE, AND YOLK.

Expt. number and condition. Fresh.	Weight of egg. Grams.	Shell. Per cent.	Yolk. Per cent.	White. Per cent.
I.....	54.3153	10.13	31.35	58.52
II.....	58.5077	9.57	30.81	59.62
III.....	54.1700	10.83	30.00	59.17
IV.....	61.9017	10.53	29.40	60.07
Average.....	57.2237	10.26	30.39	59.35
Stale.				
I.....	51.3885	11.06	33.12	55.82

The change in water content increases its rate with the temperature and diminishes with the time. The rate or the average rate from the beginning of the experiment up to any given time is merely the loss in weight divided by the time. The original weight of the white or yolk is obtained, as shown in Examples I and II, and the weight of either at any stage in the experiment can be calculated on the basis of total solids. These rates are plotted in Figs. 1 and 2. It should be stated, however, that the curves are mathematically exact and consequently are slightly more uniform than could be obtained by experiment even under the most ideal conditions. Experimental results vary above and below the values indicated by the curves, but follow them very closely in general direction.

RATE OF LOSS OF MOISTURE IN EGG-WHITE

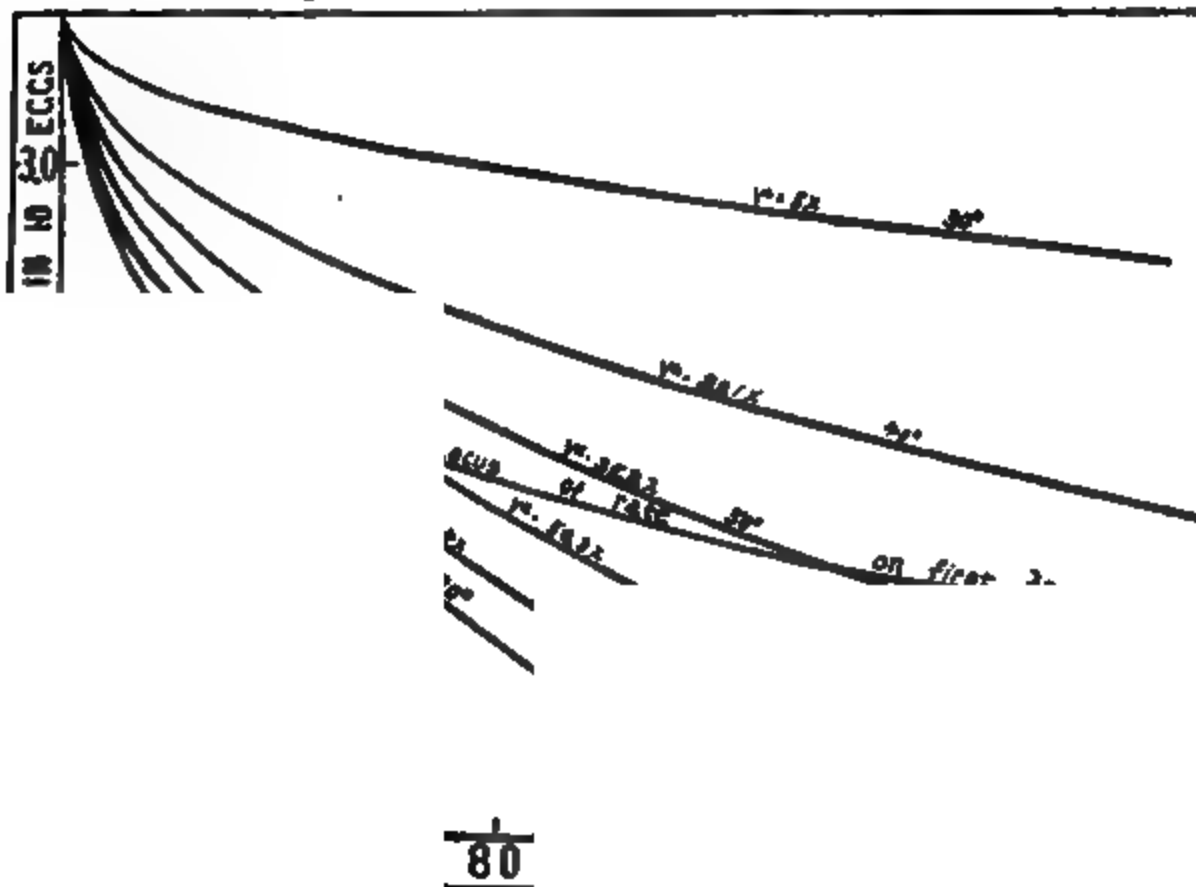


Fig. 1.

RATE OF LOSS OF MOISTURE IN EGG-WHITE

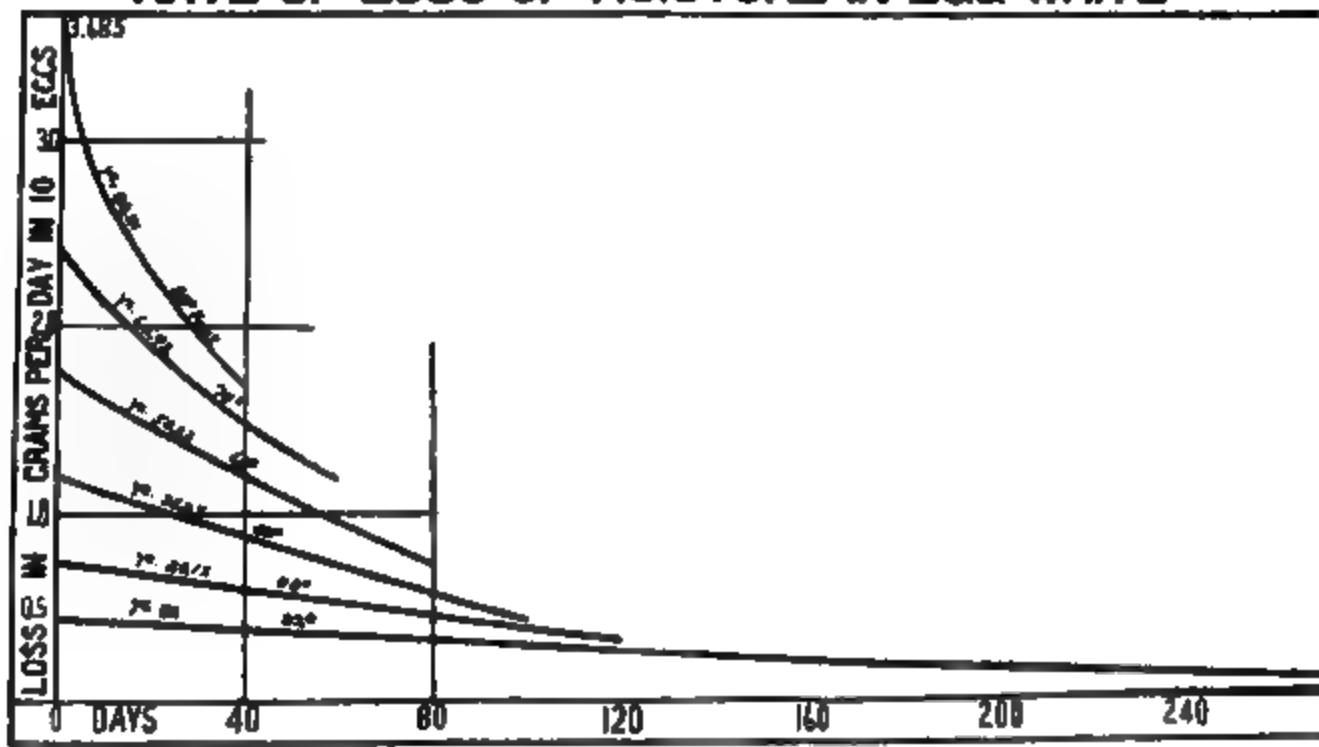


Fig. 2.

Development of the Rate Formula.

The formula is developed on the basis of the Fahrenheit scale. Days are plotted as abscissas, and grams per day or rate as ordinates. In the scale 1 unit of rate equals 20 units of the y ordinate; in the formulas y is negative and equals the distance downward from the 3.685 ordinate, or $R = 3.685 + y/20$ from which $y = -(73.7 - 20 R)$; $D = \text{days} = 2X$. The curve for the 80° experiment will take the shape of a parabola;¹ $y^2 = 80.5x$ with the axis on the y ordinate 3.685, and the vertex at $x = 0$. In order to be able to combine the curves for the different temperatures in one formula as a function of the temperature the curves must constitute a family. It is found that the 70° curve coincides almost exactly with $y^2 = 65.4x$ (if y is greater than 25.31) on the same axis, and the 32° curve in the same fashion coincides with $y^2 = 8x$ (if $y > 65$) also on the same axis. From this the following series is interpolated:

- (1) At 80° , $y^2 = 80.5x$
- (2) At 70° , $y^2 = 65.4x$
- (3) At 60° , $y^2 = 50.3x$
- (4) At 50° , $y^2 = 35.2x$
- (5) At 40° , $y^2 = 20.1x$
- (6) At 30° , $y^2 = 5.0x$
- (7) At 27° , $y^2 = 0$

giving the general formula

$$y^2 = \left(\left(\frac{t-30}{10} \right) 15.1 + 5 \right) x \quad \text{or} \quad y^2 = (1.51t - 40.3)x.$$

These are plotted in Fig. 1. The curve, however, for each temperature, does not start from $y = 0$, but from a variable origin, the locus of whose points is the parabola $v^2 = 39.1z$ ($v = \text{temperature}$ and $z = 4$ plus 50 times the rate on the first day, giving the formula $t^2 = 39.1(50 R_1 + 4)$). The parabola $v^2 = 39.1z$ is derived from a plotting of the rate for the first day at different temperatures, or R_1 .

From

$$t^2 = 39.1(50 R_1 + 4) \quad \text{or} \quad t^2 = 1955 R_1 + 156.4$$

$$R_1 = \frac{t^2 - 156.4}{1955}.$$

In order to compare the curves for the different temperatures they are all started on the same ordinate of the vertex of the 80° curve, since this vertex happens to be at $D = 0$ (Fig. 2). Then in the general formula $y^2 = (1.51t - 40.3)x$, y has the same scale value at all times ($y = -(73.7 - 20 R)$), but the value of x will be a function of the temperature.

¹ The parabolic curve was used in preference to the logarithmic, since diffusion rather than chemical action is responsible for the changes observed, and the parabola expresses in a more simple manner the facts observed.

$$x = \frac{y_1^2}{1.51t - 40.3} + \frac{D}{2} \quad y_1 = y \text{ on the first day.}$$

$$\begin{aligned} y_1 &= -(73.7 - 20 R_1) \\ &= -\left(73.7 - \frac{20t^2 - 3128}{1955}\right) \\ &= -\left(75.3 - \frac{4t^2}{391}\right) \end{aligned}$$

$$x = \frac{\left(75.3 - \frac{4t^2}{391}\right)^2}{1.51t - 40.3} + \frac{D}{2}$$

$$(73.7 - 20R)^2 = (1.51t - 40.3) \left\{ \frac{\left(75.3 - \frac{4t^2}{391}\right)^2}{1.51t - 40.3} + \frac{D}{2} \right\}$$

$$73.7 - 20R = \sqrt{\left(75.3 - \frac{4t^2}{391}\right)^2 + \frac{(1.51t - 40.3)D}{2}}$$

$$R = 3.685 - \frac{1}{20} \sqrt{\left(75.3 - \frac{4t^2}{391}\right)^2 + \frac{(1.51t - 40.3)D}{2}}$$

No experiment has been conducted at a temperature lower than 32° F., but following the order of progression in the remainder of the series y becomes zero at about 27°, indicating no transfer of water. This is also approximately the freezing point of egg material, further confirming the nonprobability of a transfer of water.

The curves in Fig. 2 are the parts of the curves of Fig. 1 below the "locus of rates on the first day," all moved back to $x = 0$. These are in fact the experimental curves, whereas the prolongations in Fig. 1 merely indicate the mathematical relation.

Application of the Formula.

By means of the rate formula and one analysis of a sample of eggs it is possible to predict the condition of the eggs at any temperature for any given date within a reasonable holding period. The rate multiplied by the time gives the loss in weight, from which data it is a simple matter to find the percentage of moisture remaining.

The curves are all on the loss of water in the white. Similar results are obtained by plotting the rate of increased moisture in the yolk. More extensive work along this line is now being done.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

STUDIES ON WATER DRINKING. XII. ON THE ALLANTOIN OUTPUT OF MAN AS INFLUENCED BY WATER INGESTION.¹

BY L. T. FAIRHALL AND P. B. HAWK.²

Received February 10, 1912.

Introduction.

The allantoin literature was reviewed in a recent article from this laboratory.³ Very little work on allantoin has appeared in the scientific press since that time. The recent work of Hunter and Givens⁴ is of particular interest. They used monkeys as subjects and isolated the allantoin from the urin of the animal by the method of Wiechowski. They could detect no uric acid and found only 4.5 mg. of purine base nitrogen in 500 cc. of urin. The same authors have just reported further findings on the normal purine metabolism of the monkey.⁵ They found that 71-87% of the total purine nitrogen appeared as allantoin. When sodium nucleate was fed, sometimes as much as 90% of it was recovered, for the most part as allantoin. It is evident, therefore, that the monkey possesses a uricolytic enzyme which splits uric acid into allantoin. An analogous condition has not, thus far, been definitely demonstrated for the human organism. Schittenhelm and Wiener,⁶ for example, after feeding nuclear material failed to observe what they considered to be an increased output of allantoin. The allantoin output in these instances was small, to be sure, but nevertheless the authors mentioned present no data from control periods for comparison. We cannot be certain, therefore, that the allantoin output, though small, *was not increased* under the influence of the feeding of the nuclein-bearing material. Moreover, the subjects used were clinical patients and it is quite possible that their metabolic attitude toward the ingested material was not that of a normal organism. The finding by Ascher⁷ of allantoin in the urin of a fasting man indicates that in the human organism, as well as in that of the lower animals, allantoin may have an endogenous origin. Objections have been raised to such an interpretation on the basis that the fasting period in Ascher's experiment was not long enough to insure the non-influence of the feeding period upon the allantoin output.

¹ Reported before Am. Soc. Biol. Chem., Baltimore, December, 1911.

² The authors wish to thank Mr. L. A. Fritze for assistance rendered during the early stages of the allantoin determinations.

³ Wreath and Hawk, *THIS JOURNAL*, 33, 1601 (1911).

⁴ *Am. J. Physiol.*, 27, 1911.

⁵ Reported before Soc. Biol. Chem. and Biological Section Am. Chem. Soc., Washington, December, 1911.

⁶ *Z. physiol. Chem.*, 63, 283 (1909).

⁷ *Biochem. Z.*, 26, 370 (1910).

ALLANTOIN EXCRETION AS INFLUENCED BY WATER INGESTION.

Days.	Water ingested. Cc.	Allantoin excreted Gram.
Fore period:		
13.....	900	0.0135
Water period:		
1.....	3450	0.0173
2.....	3450	0.0166
3.....	3450	0.0157
4.....	3450	0.0162
5.....	3450	0.0205
Average.....		0.0173
Final period:		
5.....	900	0.0122

Certain perfusion experiments of Ackroyd¹ are of interest. This investigator found that when sodium urate was perfused through the surviving liver of the dog that a portion of the urate was destroyed. Only part of the destroyed urate was recovered as allantoin. In later experiments of this character in which rabbits were used as subjects, it was found that the urate was converted quantitatively into allantoin.² Ackroyd has examined certain foods for allantoin, and reports that milk, white bread, French peas and green peas all contain allantoin in small amount, whereas more could be detected in eggs, bananas or rhubarb.³ The failure of Schittenhelm and Wiener⁴ to find any allantoin in the urine of a subject maintained upon a diet of milk and vegetables permits of the query as to whether the urinary allantoin excretion is influenced by the allantoin which forms a constituent part of the ingested food. This question has been partly answered by further work of Schittenhelm and Wiener,⁵ in which it was shown that only 30% of the allantoin ingested by human subjects in the form of an aqueous solution was recoverable in the urine.

Experimental.

It was proposed to demonstrate what influence, if any, would be exerted upon the urinary allantoin output of a normal man when he was caused to ingest large quantities of distilled water at meal time. The subject of the experiment was a man weighing 57.5 kg. The plan of the investigation was the same as that utilized in this laboratory in connection with previous water-drinking researches.⁶ The experiment was

¹ *Biochem. J.*, 5, 217 (1910).

² *Ibid.*, 5, 442 (1911).

³ *Ibid.*, 5, 400 (1911).

⁴ *Loc. cit.*

⁵ *Z. physiol. Chem.*, 63, 287 (1909).

⁶ Fowler and Hawk, *J. Exp. Med.*, 12, 388 (1910). Mattill and Hawk, *THIS JOURNAL*, 33, 1978 (1911); *Ibid.*, p. 1999; *Ibid.*, p. 2019.

divided into three separate periods, a fore or control period, a water period and a final period. The following uniform diet was fed each day throughout the experiment: 300 grams graham crackers, 1200 grams whole milk, 75 grams butter, 45 grams peanut butter. Thirteen days were included in the fore period and five days in the final period, and during each of these days 900 cc. of water were ingested, 300 cc. of it being taken at meal time. The water period was five days in length and on each day of this period 3450 cc. of water were taken, 2850 cc. of this volume being taken at meal time.

The method used for the determination of allantoin was that proposed by Wiechowski.¹

Discussion.—The analytical data are summarized in the table on page 547. It will be noted that the average daily excretion of allantoin for the thirteen normal days preceding the interval of high-water ingestion was 0.0135 gram. Upon the first day of the water period when the ingestion of water was increased from 900 cc. per day to 3450 cc., the allantoin output rose to 0.0173 gram and remained above normal throughout the five days of copious water-drinking. The values for the remaining four days were 0.0166, 0.0157, 0.0162 and 0.0205 gram, respectively. The average daily allantoin excretion for the entire water period was 0.0173 gram, which happens to be the identical allantoin value as determined for the initial day of the period. This constitutes an increase of over 20% above the normal allantoin level. At the opening of the final period, during which the water ingestion was reduced to the normal quantity, the daily allantoin output decreased very perceptibly from that observed during the water interval. The average daily output for this final period of five days was 0.0122 gram. It will be observed that this is a decrease of about 30% from the values determined for the water period. It is also somewhat lower than the value as determined for the fore period. This same compensatory effect has been noted in our water experiments in other connections. In other words, when a certain urinary constituent is increased under the influence of a high water ingestion it very often happens that the output of this constituent is sub-normal in the succeeding period. On the other hand, if the constituent has been excreted in sub-normal amount during the water period the post-water interval will many times witness an augmented excretion.

We realize fully that we are dealing here with very small quantities of allantoin. However, inasmuch as we were feeding our subject a diet which was absolutely uniform from day to day we feel justified in concluding that the water, when given in increased quantity, caused an augmentation in the daily allantoin output. We would interpret this find-

¹ Wiechowski, *Biochem. Z.*, 19, 368 (1909).

ing, tentatively, as indicating that the oxidative functions of the organism have been stimulated through the passage of this large volume of water into the organism in question and consequently material of purine origin which would under ordinary conditions have been excreted in other less highly oxidized forms was oxidized to allantoin and eliminated as such (see Summary). In support of this interpretation, we would cite certain other findings reported from this laboratory. In the experiments in question¹ the uric acid output of a normal man living on a normal uniform diet was found to undergo a pronounced decrease when large quantities of water were ingested. At the time this finding was reported, we found it difficult to see "how an increased water ingestion could be considered as a logical forerunner of a *decreased* uric acid excretion." When an *increased* allantoin output was subsequently obtained in an experiment entirely similar in character and also made upon a human subject, the possibility of the interrelationship of these two findings suggested itself to us. It should be mentioned that in the work on uric acid elimination, to which reference has just been made, a large part of the decrease in the output of uric acid was believed to be due to the fact that the method employed (Folin) for its determination was not entirely satisfactory for use in connection with the *dilute* urines of the water period.

Several arguments may be advanced against the validity of our interpretation. In the first place, Ackroyd's² demonstration that various food products contain allantoin may be considered by some to eliminate the possibility of interpreting our increased allantoin as of endogenous origin. In the second place, the failure of Schittenhelm and Wiener³ to secure a high allantoin output after the feeding of purine material is considered evidence that uric acid is not oxidized to allantoin in the human organism. The findings of Ackroyd to our mind do not constitute a valid objection to our interpretation inasmuch as we were feeding a *uniform diet* and if the food fed did contain allantoin identical quantities of allantoin must of necessity have been ingested daily. And under such conditions the water period witnessed an *increase* in the excretion of allantoin. Much of the force of Schittenhelm and Wiener's findings as furnishing evidence against our interpretation is lost because of the fact that their feeding tests were not adequately controlled and the subjects were not *normal* individuals. On the other hand, an observation which furnishes strong proof of the endogenous origin of allantoin in the human organism is Ascher's finding of allantoin in the urin of a fasting man. More observations on subjects fasting for longer intervals are, however, essential.

¹ Rulon and Hawk, THIS JOURNAL, 32, 1686 (1910).

² *Loc. cit.*

When one considers the ease with which uric acid may be oxidized to allantoin *in vitro*, and the further fact that a similar transformation occurs in the organism of lower animals, it is logical to look for at least some oxidation of this character in the human organism.

Summary.

When the diet of a normal man was supplemented by 900 cc. of water per day the average daily output of allantoin (Wiechowski's method) was 0.0135 gram for a period of thirteen days. Upon increasing the water intake to 3450 cc. per day for a period of five days, the average daily allantoin excretion was increased to 0.0173 gram. This constitutes an approximate 20% increase. The daily value for a five-day final period on the original 900 cc. water ingestion was 0.0122 gram.

The increase in the allantoin output accompanying water-drinking may indicate that the oxidative mechanism of the organism has been stimulated through the introduction of the large volume of water into the body and that purine material which would ordinarily have been excreted in some less highly oxidized form has been oxidized to allantoin and excreted in this form. This interpretation is strengthened by the finding in this laboratory of a decreased uric acid output after the water ingestion of the subject (man) had been considerably increased.

In view of the fact that the above interpretation is contrary to the current views regarding purine metabolism in the human organism, the authors make the interpretation tentatively until further experiments may be completed.

URBANA, ILL.

A NEW APPARATUS FOR VACUUM SUBLIMATION.¹

BY GEORGE W. MOREY.

Received February 9, 1912.

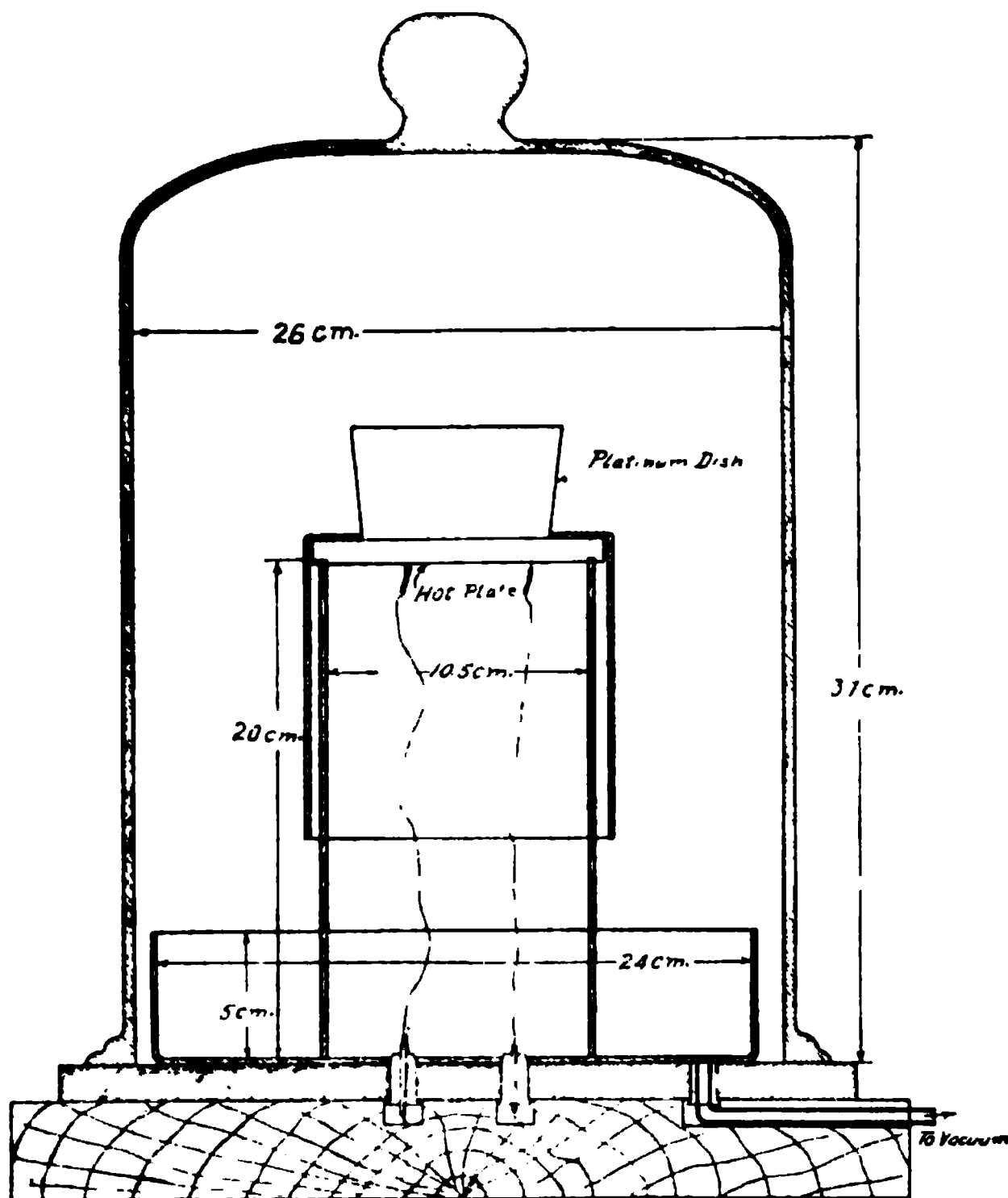
An examination of the literature shows surprisingly few descriptions of apparatus for sublimation *in vacuo*. The apparatus of Kempf² is probably the best of the common forms. It is easily broken, however, since one of the ground joints becomes heated, both by radiation and by the condensation of the sublimed material. Moreover, it is not suitable for working with large quantities of material.

The need arising to sublime large quantities of certain organic compounds, the apparatus described here was devised. Its construction can be readily seen by referring to the sketch. The bell jar is a large one (26 cm. diameter) and the joint between it and the glass plate is well ground, so that it will readily hold a vacuum with a very thin coating of

¹ Published by permission of the Director of the Bureau of Standards.

² Richard Kempf, "Praktische Studien über Vakuum-sublimation," *J. prakt. Chem.*, **78**, 201-59.

stopcock grease. Since this joint is never heated and none of the sublimed material comes in contact with it, no contamination is to be feared. A large, shallow crystallizing dish, that will just sit inside the bell-jar, rests on the glass base plate, and on it rests a glass cylinder, 10.5 cm. in diameter and 20 cm. high, cut from a large piece of tubing. This glass cylinder serves as a support for the electrical heating element, which is of the type ordinarily used in electrically heated hot plates, with an iron top and an enamel bottom. The top of the cylinder is loosely ground into the enamel bottom of the hot plate. The glass cylinder also serves



to keep the sublimed material from coming in contact with the lead wires or with the top of the rubber stoppers. The wires carrying the current are led in through the bottom as shown, the rubber stoppers being pushed in far enough to pass through the holes in the crystallizing dish, thus holding the latter in position. It is best to have the wires in two parts with connectors near the top, to facilitate the removal of the heating element. The substance to be sublimed is placed in a flat bottomed platinum dish or in a crystallizing dish resting directly on the hot plate. A deep crystallizing dish, with a hole cut out through the bottom to receive the platinum dish, is placed, upturned, over the top, as shown, to

prevent the sublimed substance coming in contact with the iron hot plate. The bell jar is evacuated through the bottom, the crystallizing dish not being drilled in this case. The whole is mounted on a wooden base, cut out to allow the electrical leads and vacuum connection to pass through.

The advantages of this form of apparatus can be readily seen. It is convenient, since lifting off the bell jar renders all parts readily accessible. Most of the sublimed material drops into the crystallizing dish, from which it can be easily removed. This materially affects the speed. In most forms of sublimation apparatus the solid is condensed directly above the unsublimed portion, and all that drops must be re-sublimed, with no consequent gain in purity. The material comes in contact with nothing but glass and platinum. This is unimportant with stable substances such as naphthalene, but with easily decomposed substances such as salicylic acid it is important. The apparatus can be readily calibrated so that the approximate temperature can be determined by having an ammeter in the circuit.

The above apparatus for vacuum sublimation has been in use at the Bureau of Standards for over a year, during which time it has given complete satisfaction in the last step in the purification of the naphthalene and benzoic acid issued by the Bureau as standard calorimetric samples. It is rapid and efficient, the process is under complete control, and the apparatus requires but little attention.

NOTES.

An Improved Extraction Apparatus.—The extraction apparatus here illustrated and described was designed early in the year 1909 for special use with a number of unusual solvents, but has since been employed quite extensively in the laboratories of this Bureau for general purposes. It represents the result of an attempt to combine in an all-glass device the principal advantages of the Wiley and Soxhlet forms. It was desired to make a compact, convenient apparatus free from stoppers, seals and ground connections, the separate parts of which should be simple and interchangeable as well as readily accessible for cleaning, alteration or repair.

It consists of three essential parts, a straight outer tube A, a condenser, B, terminating at the lower end in a small glass hook, and a suitable extraction tube, C, for holding the material to be extracted. The extraction tube (shown in perspective) is suspended from the hook on the condenser by means of a semi-circular wire bail of such a size that it may be swung out of the way when filling or emptying the tube. While it may readily be adapted to meet any special requirements, it is usually

provided with a siphon for intermittent drainage. The siphon, however, need not be an integral part of the tube, since a separate siphon of small bore hung over the edge of a plain tube is generally found to fill by capillarity and operate with entire satisfaction.

A convenient size of the apparatus for use with such solvents as alcohol, acetone, or chloroform consists of an outer tube 4.5–5.0 cm. in diameter and 24–25 cm. in length with other parts proportioned about as indicated in the sketch. Glass naturally presents a somewhat less effective cooling surface than metal, so that for the more volatile solvents the condenser, as illustrated, is rather short. In winter or when specially cooled water is available, however, even this very short condenser will retain ethyl ether without excessive loss.

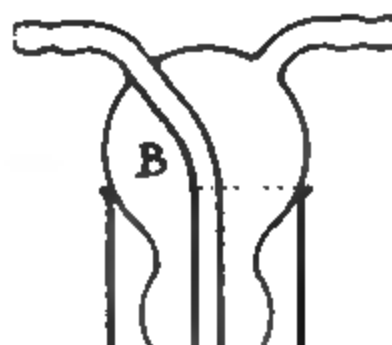
If it is desired to weigh the substance removed by the extraction, it is convenient to rinse the contents of the outer tube into a tared dish of appropriate size for evaporation. Where the extract is to be treated further without weighing, the comparatively large mass and capacity of the tube are not found to be objectionable.

It should be noted that the contents of the extraction tube are maintained at a temperature but slightly below the boiling point of the solvent. This is generally considered to be an advantage, but has the effect of preventing the use of the apparatus as described with non-homogeneous solvents such as petroleum ether, since the more volatile constituents tend to collect and boil in the extraction tube, while the siphon is superheated by the vapors of the higher boiling components and thereby rendered inoperative.

THOS. B. FORD.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A Modified Jacket for a Victor Meyer Vapor-Density Apparatus.—When any considerable number of students are engaged in the determination of molecular weights by the Victor Meyer method, the breakage of outer jackets is a source of constant annoyance. These jackets are rather expensive, are easily broken, and the blowing of a new bulb is usually beyond the skill of the student. A simple device illustrated in the drawing has been found to be quite satisfactory as a substitute for these jackets



A plain beaker, *A*, takes the place of the bulb. It is provided with a copper cover, a cross-section of which is shown at *B*. The collar in the center should be of such size that the smallest tube which is to serve as a jacket will readily slip over it. The deep groove around the collar, made broad enough to take the widest tubes, serves as a water seal for connecting the outer jacket *C*. The liquid condensing on the walls of the outer tube automatically fills this seal, and the collar should be provided with several small drain holes just below the level of the flat cover to prevent the liquid from overflowing the seal. It is not necessary to connect the cover with the beaker. If the cover is flat, and the rim of the beaker reasonably true, the surface tension of the film of liquid at the joint prevents any appreciable leakage as there is very little pressure upon it. The tube *C* may be made from a broken outer jacket or from any tubing of suitable size. It is cut square at both ends and its length is readily adapted to that of any inner tube. If desired, the beaker may be replaced by a metal can or spun bulb provided with the arrangement for a water seal, and the cover could be manufactured from porcelain or glass instead of sheet copper.

W. E. HENDERSON.

OHIO STATE UNIVERSITY.

CORRECTION

In the article by Bogert and Heidelberger in the February number of *THIS JOURNAL*, 34, 183, there occurs a confusing error which should be corrected. On page 188, the concluding sentence of the second paragraph reads: "It seems odd that the phthalone should form a salt with phthalic and not with the strong mineral acids." This sentence should be eliminated, since the compound to which it refers, and with which the rest of the paragraph deals, is not a phthalate of the *phthalone* but of the *quinazalone*.

M. T. BOGERT, M. HEIDELBERGER.

NEW BOOKS.

Hilfsbuch für Nahrungsmittelchemiker. By A. BUJARD AND E. BAIER. Third Edition. 8vo. pp. xviii + 730. Price, 12 M.

The scope of the book is not confined, as the title would indicate, to the examination of foods. It also includes tobacco, water, air, soil,

tanning material, urin analysis, and fifty pages are devoted to bacteriology.

The first edition of the book was warmly welcomed. The literature relating to the examination of foods and especially food adulteration for the most part could only be consulted in the original articles in the journals. Few reference books handled the subject in anything like an adequate manner. The work of Bujard and Baier appearing at this time presented an exceptionally valuable compilation of the methods then available.

The present edition does not appear to represent the literature on that subject to-day as well as the first edition did at the time of its publication.

The book is of special value, however, as a work of reference in the subjects that are ordinarily handled in several volumes but does not go into the detail often necessary in the investigation of a particular class of foods. The methods do not always include the latest ones published which have been found valuable for the examination of the products under discussion. For instance, the Roese method is still described for the determination of fusel oil in distilled liquors. The necessity for the examination of added oil in paprika is not recognized. The refractometer method for the detection and determination of methyl alcohol is not given. Sjerning's method for the separation of peptones and meat bases is not given.

Unfortunately the authors do not appear to have consulted the literature in other languages than their own.

The recent contributions of American laboratories which have made possible the adequate inspection of the foods on the market in this country are entirely overlooked with the exception of brief references to a very few abstracts appearing in German journals. Notwithstanding the enormous importance of German writers to the literature of food chemistry it is no longer possible for an author to treat the subject adequately and ignore the contributions of American laboratories.

W. D. BIGELOW.

L'Internationalisme Scientifique (Sciences Pures et Lettres). Par P. H. EIJKMAN. Médecin à La Haye. Publication du Bureau Préliminaire de la Fondation pour L'Internationalisme. La Haye. 1911. Price, three francs.

There are now so many international organizations, that, as Professor Schuster said five years ago, we must begin to guard against overlapping and future conflict. The Bureau Préliminaire de la Fondation pour L'Internationalisme has attempted to secure adequate information about every organization within certain limits which is fairly to be called international. This information is preserved in the "Archives et la Bibliothèque de l'Internationalisme." By means of a detailed and complete survey of international activities, it hopes to aid each new undertaking to avoid duplication and consequent division of forces.

In 1910, the Bureau published "L'Internationalisme Médical," giving information concerning more than two hundred enterprises connected with medical science. The present work contains a dozen pages of supplement to the publication of 1910, and then describes organizations having to do with Science and Letters, or with Science, or with Letters; letters is made to include linguistics and literature, and also history, art, philosophy and theology.

After 6 + xii + 108 pages of text, a larger number of unnumbered pages are filled with information concerning every international organization known to the Bureau, in a form available in making up card catalogs.

EDWARD W. MORLEY.

Opere Scelte di Amedeo Avogadro. Publicate dalla R. Accademia delle Scienze di Torino. Torino: Unione Tipografico-Editrice Torinese. 1911. Quarto, pages 6 + cxi + 491. Price, 20 lire.

Count Amedeo Avogadro was for more than fifty years a member of the Royal Academy of Sciences at Turin, honored for distinguished attainments in science and loved as a man. When he passed away in 1856, the Academy provided a suitable commemorative discourse.

The year 1911 was the centennial of the publication of the first of the five great memoirs in which Avogadro's law was announced and supported and applied. Worthily to commemorate one of the most important achievements yet made in chemistry, the Academy in 1907 named an Executive Committee which has obtained a bronze bust of Avogadro and has provided for the publication of this selection from Avogadro's published memoirs.

The execution of the task is worthy of the Royal Academy and of the memory of Avogadro. The paper is of high quality; each page bears as a watermark the name *Amedeo Avogadro*; the type and presswork are excellent. It contains, first, a note by the president of the Academy; then, a portrait of Avogadro from the new bronze bust; a historical and critical discourse on the life and scientific work of Avogadro; reprints of his papers on the molecular constitution of gases, on electricity, on electrochemistry, and on capillarity; and a bibliography. Out of the 55 papers and books there listed as having been published, twelve are reprinted in full in this volume.

[The Italian physicist Botto wrote an account of the life and scientific works of Avogadro soon after the death of the latter; there seems to have been no more extensive biography until Guareschi, in 1901, published his "*Amedeo Avogadro e la teoria molecolare*," in 47 quarto pages. Together with this memoir appeared a translation into Italian, by the daughter of Guareschi, of that paper of Avogadro which is most frequently cited, which had been published in 1811 in French, and which had never before been printed in Italian. It was natural that Guareschi

should be chosen to edit the present volume, and the choice was a happy one. The historical and critical discourse fills 140 pages. It is well written and clear. Some ten pages tell of Avogadro's life, about a hundred tell of the law named after Avogadro and of its applications, and some thirty pages describe Avogadro's other scientific work or contain documents concerning incidents in his life.

Avogadro's law is now regarded as the corner stone of the whole edifice of chemistry, and Avogadro's name is forever inscribed on it, alone. Only the older of chemists now living remember when it was called the law of Ampère and Avogadro. All of us have some knowledge of the fact that, although published in 1811, it was not generally accepted and generally regarded as important till forty or fifty years later, and that the experimental explanation of apparent exceptions, like that shown by ammonium chloride, needed even twenty years more. Nearly all of us know how the labors of Gerhardt and the voice of Cannizzaro were most influential in securing the general adoption of the law of Avogadro.

The fate of the law during the years before 1850 or 1860 makes a curious story. It was published by an Italian who was a French subject, in a French journal, before the great preeminence in chemistry had passed from France. But a rediscovery of the law by Ampère was published in the same journal within three years. During the next ten years, Avogadro had developed the consequences of his law in four following memoirs, and had arrived at formulas for many common or important compounds which agree with those adopted now. That these were not at once adopted by other chemists in place of those of Berzelius is not strange; but when Gerhardt, by the use of other methods, had come to similar formulas, and when physicists like Clausius had accepted the law, one could fairly presume that Avogadro would be honored for an important scientific service. Yet the Italian physicist who wrote in the *Nuovo Cimento* an account of the life and work of Avogadro at the time of his death did not mention the great law named after him. When in the next year a bust of Avogadro was unveiled at the University of Turin, no chemist spoke in his honor, and the physicist who spoke did not mention the law which is his chief title to remembrance.

After 1880, Avogadro's law was generally accepted, but often attributed to others. Wurtz, in 1864, named it the law of Ampère; in 1867, he expressly asserted "Ampère announced it first;" in 1868, he named it the law of Avogadro and Ampère; not till 1879, did he name it correctly. P. G. Tait, about 1870, attributed the law to Gay-Lussac. Some Italian chemists, between 1860 and 1875, attributed the law to Ampère or to Dumas.

The law was sometimes misstated, even by eminent chemists. Wurtz, in a lecture in 1863, spoke of the "celebrated assertion of Ampère and

Berzelius that equal volumes of gases contain equal numbers of *atoms*." When the law was rightly stated, its discovery was attributed to the study by Avogadro of the compressibility and expansion of gases, while the discoverer ascribed the discovery to the study of Gay-Lussac's observations on combining volumes. Some eminent American chemists have fallen into this error. It is true that Dumas, in the well known passage where he expounds the law, mentions compression and expansion, but he has in mind logical relations and not a history of origin.

The long neglect of the law and of its discoverer, and the subsequent mistakes as to its nature or its discoverer, are the occasion of an important chapter in Guareschi's discourse, entitled "Avogadro forgotten." In this are discussed the reasons for such a state of things. One reason was, the general failure to distinguish between atoms and molecules. Another, the fact that Avogadro was not known as an experimental chemist. An important cause lay in the political conditions of Italy, a country which Lamartine called *the land of the dead*. Up to the year 1840, against the great names of chemists in France, England, Germany, and Sweden, Italy could set but two names, those of Berthollet and Avogadro—and one of these was drawn from Italy to Paris. The state of the science also delayed the appreciation of the law; both Berthollet and Avogadro opened paths from which chemists were for a time diverted by matters more urgent or more immediately profitable to the science.

The discussion of these reasons, as well as of six more following, make this chapter especially interesting. Other chapters of especial interest are those which show how clearly Avogadro conceived and explained the distinction between atoms and molecules, how well he understood that property of atoms which we now call equivalence or valence, and how exactly his system of molecular formulas agrees with that used by all of us to-day. The book ought by all means to be accessible at every center of chemical instruction.

EDWARD W. MORLEY.

L'Annuaire du Bureau des Longitudes pour l'année 1912. 16mo., 750 pages. Price, post-paid 1 fr., 85 (\$0.36). Paris: Gauthier-Villars.

The volume contains 324 pages of physical and chemical tables, certainly a great deal for the money. There are some glaring inaccuracies, and very few of the tables contain any data determined within the last ten years. They may be recommended as 'better than none at all,' to those who have not sufficient money to buy better ones.

J. W. R.

Physico-Chemical Calculations. JOSEPH KNOX. Methuen & Co., London. pp. 186. Price, 2s. 6d.

This book is intended to supplement the text-books of physical chemistry for class use. It is based upon Abegg and Sackur's "Physikalisch-Chemische Rechenaufgaben" but in the process of translation has been

rearranged and much enlarged. Each chapter has a short introduction giving definitions and the more important laws of physical chemistry expressed in mathematical form but not derived. This is followed by a few numerical problems (74 altogether) solved in detail and a larger number of problems to be solved by the student (291), the answer being given in each case. The author states that most of the problems have been taken from the literature but references are not given. A knowledge of calculus is assumed but very few of the problems given require the use of calculus. The section on thermochemistry would be improved by the inclusion of problems involving the influence of temperature on the heat of reaction as a function of the heat capacities of the factors and products. The van't Hoff equation $d\ln K/dT = Q/RT^2$ is integrated only on the assumption that Q is independent of the temperature. The resulting equation is used over a temperature range of 400° in one case. Similarly the only form of the free energy equation given involves the assumption that Q is independent of temperature. The section of the book dealing with the solubility product should be used with caution and rewritten in later editions in the light of very recent work (Noyes, Bray, Harkins, *et. al.*, THIS JOURNAL, Nov. and Dec., 1911). The book will undoubtedly increase the amount of problem solving done by students in courses in physical chemistry and therefore serve a valuable purpose.

GRINNELL JONES.

Magnetochemie: Beziehungen zwischen magnetischen Eigenschaften und chemischer Natur. PROF. DR. E. WEDEKIND. 110 pp. Mit 25 Text-abbildungen. Berlin: Gebrüder Bornträger. 1911. Price, 4 Marks.

The author has rendered a real service to those interested in magnetism, whether as physicists or chemists, in that he has collected and coördinated a mass of widely scattered and frequently conflicting observations. These he has systematized and arranged under the heads of ferromagnetic, paramagnetic and diamagnetic materials. He discusses the relation of the magnetic properties of the elements to their atomic weights and shows them to be a periodic function of the latter.

The magnetic properties of the alloys of nonmagnetic elements, the magnetic properties of compounds both inorganic and organic, and the influence of both high and low temperatures are discussed.

There are also presented an introductory chapter defining magnetic magnitudes and a brief description of methods of investigation and a closing chapter on the "Magnetonen" theory of Weiss. Unfortunately, from the viewpoint of the writer, the author does not introduce a chapter on the chemical effects of magnetism, references to which are so widely scattered through both physical and chemical literature. A collection of these observations would make very interesting reading.

The author appends a foot-note to his preface in which he asserts that

he has thoroughly reviewed the literature up to October 15, 1911. While the text is filled with references to original literature not one is to an American contribution. While the writer is not in a position to discuss the merits of the case he has in his possession a list of some forty-five contributions in American journals some of which are of indubitable value. We fear the oversight is simply another evidence of continental provincialism.

H. G. BYERS.

Analytical Chemistry. Volume II, Quantitative Analysis. By F. P. TREADWELL. Third English Edition. Translated by William T. Hall. pp. xi + 903, 126 figures. 1911. New York: John Wiley & Sons. Price, \$4.00.

The revised and enlarged edition of Professor Treadwell's admirable book will certainly receive a hearty welcome from all chemists. In the effort to prepare "a book which will be useful to English-speaking students" Professor Hall has done more than simply translate the German edition.

The printing of the text is uniformly well done, but the same cannot be said of all the illustrations. Only a few typographical errors have escaped the proof-reader, but the form "different * * * * * than" used twice on page 538 cannot be commended.

The book is differentiated from similar books by the unusual amount of detail regarding electrolytic methods of analysis and especially by the full treatment of gas analysis.

Among the later developments in analytical chemistry there is noted the determination of nitric acid as nitron nitrate, of nickel as nickel glyoxime and the use of the electric furnace for ignition of crucible contents. A colored chart of arsenic standards accompanies the description of Sanger's method for determining arsenic.

Physico-chemical considerations are noted in the discussions of the solubility product and the distribution coefficient. CHAS. H. HERTY.

Theorie und Praxis der Maassanalyse. VON ALEXANDER CLASSEN. Leipzig. 1912. pp. 772. Akademische Verlagsgesellschaft, M. b. H.

With the object of embodying the theory of a science and its practical application in one production, Professor Classen has conceived and executed a masterly piece of work. The book is, however, more than its title claims it to be. Not only are the theoretical principles underlying every method illustrated by equations and explained by discussions, but the history of some of the older methods is also given and the merits of the various modifications they underwent critically and thoroughly discussed. The various theories advanced towards the explanation of the role played by catalyzers, as for instance manganese sulfate in the titration of iron with permanganate in the presence of hydrochloric acid, are quoted and the evidence for and against them weighed. As an ex-

ample of the fulness of the treatment, Volhard's method for the estimation of manganese occupies twenty-seven pages, the determination of silver twenty-two and that of zinc eighteen.

A point of special merit in this book is that the reason for every step in an analysis is given. The analyst is thus enabled to understand what he is doing and why.

The subject of standardization of solutions receives considerable attention, and much stress is laid on the choosing of the "primary substance (Ursubstanz) with which solutions are to be standardized."

The book is divided into five chapters: introductory, alkalimetry and acidimetry, oxidimetry, iodometry and precipitation analysis. The introductory chapter extends over one hundred and seven pages and deals with the principles of volumetric analysis, theory and descriptions of indicators and the calibration of volumetric apparatus. The Köttschtorfer saponification and Reichert-Meisel numbers determination is found in the chapter on alkalimetry and acidimetry, the iodine number of oils and fats under iodometry and hardness of water and the estimation of reducing sugars are included in precipitation analysis.

While methods for the estimation of some of the rarer elements and substances, such as cerium, thallium, selenous and tellurous acids, are incorporated in this book, none are given for the technically important metals, lead and arsenic. Of the several excellent methods for the volumetric determination of manganese, only Volhard's is considered, the others are not even mentioned.

By reason of the method of treatment of the subject, the reading of this book, aside from being profitable, is, unlike that of most text-books, very enjoyable. We are sure that the volume will be welcomed by the student of chemistry as well as by the practical chemist. J. ROSIN.

The Identification of Organic Compounds. By G. B. NEAVE, M.A., D.S.C., and I. M. HEILBRON, Ph.D., Lecturers and Demonstrators, Department of Chemistry, Glasgow and West of Scotland Technical College. 103 + viii pp. New York: D. Van Nostrand Company. Price, \$1.25.

The authors have attempted in this volume to bring together in a convenient form the principal reactions and physical constants of the most important organic substances, in such a way that by the use of it the identification of simple organic compounds may be easily accomplished. It is presumed that students in a course on the identification of organic substances are already somewhat experienced in organic chemistry.

The book is divided into thirty-four "sections." The first gives certain preliminary tests, the second the tests for the elements, the third takes up various "group reactions," such as the test for an aldehyde, amino group, etc., then follow sections on hydrocarbons, alcohols, ethers, and so on, the most important organic groups each occupying a

section. In each section are included the general properties and principal reactions of the group under consideration, together with a list of the more important members. For example, Section XXI deals with amines. The general properties are given, then the action of nitrous acid. A list of twelve aliphatic amines follows, but merely the formulas and melting points or boiling points are appended. Next, aromatic amines are considered, the tests explained, and a list of seventeen members briefly described. Finally eight halogen amines (such as *o*-chloraniline) are mentioned, the melting point of the amine itself and of its acetyl compound being given in each case. This section is fairly representative.

Some students may find this book useful, but the reviewer is of the opinion that the identification of organic substances is not a simple enough affair to permit of adequate treatment in a book of this size.

LATHAM CLARKE.

A Text-Book of Physiological Chemistry. By OLOF HAMMARSTEN. Authorized Translation from the Author's Enlarged and Revised Seventh German Edition. By JOHN A. MANDEL. Sixth Edition. New York: John Wiley & Sons. Price, \$4.00 net.

This standard book has been enlarged and changed rather more than in previous editions. A new chapter from the pen of S. G. Hedin on Physical Chemistry in Biology has been added, dealing with osmotic pressure, colloids, catalysis, enzymes, ions and salt action. Its introduction has necessitated extensive rearrangements. The chapter on the Animal Cell of the previous edition has been eliminated while its subject matter has been distributed. Thus the nucleic acids, the purine and pyrimidine bases are treated with the nucleoproteins, and the lipoids with the fats. The result is not merely to systematize the material but vastly to increase the readability. Many of the chapters have been extensively rewritten so that very little important new work remains unconsidered. This is particularly noticeable in the treatment of proteins and of absorption. Not merely have well established new facts been incorporated but often hypotheses still under discussion have been treated in an objective and judicial way that is most illuminating. Some subjects, however, are declared not yet ripe for discussion. This is a matter for regret since the author has the gift of clarifying such subjects by impartial discussion. As the result of the present great activity in biochemistry the volume has again grown in size by more than one hundred pages, and has thus developed into a book of the greatest usefulness to the advanced student although it has, perhaps, become too large and detailed to serve as an introduction to the subject.

CARL L. ALSBERG.

THE JOURNAL
OF THE
American Chemical Society

ON THE DENSITY OF SOLID SUBSTANCES WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.

BY JOHN JOHNSTON AND L. H. ADAMS.

Received March 7, 1912.

To many it may seem that a paper at this time on the density of solids is superfluous, in view of the large amount of work which has been done on this subject heretofore. But any one who studies the voluminous literature pertaining to the subject will find that our knowledge of the true specific gravity of many pure solid substances is still far from satisfactory; for the reason, namely, that the density of a solid is really much more an individual property of the particular sample of material used than a general property of the chemical substance. This is especially evident from the work of Kahlbaum, Roth and Siedler¹ on the specific gravities of certain metals. As an example, we may take copper, for which in the tables of Landolt-Börnstein-Meyerhoffer, we find the following densities given:

Copper, cast.....	density = 8.300-8.921
Copper, wire.....	8.930-8.949
Copper, hammered.....	8.919-8.959
Copper, electrolytic.....	8.884-8.952

with a general mean value of 8.933. Now the very careful determinations of Kahlbaum gave for pure distilled copper the value 8.9326, which after pressing to 10,000 atmospheres for 11 hours had increased to 8.9377; which, in turn, diminished again to 8.9317 after 1 hour at 20,000 atmospheres pressure. From the foregoing, it is evident that the density of a substance so common as metallic copper is known only to the second

¹ *Z. anorg. Chem.*, 29, 197, et seq. (1902); *Verhandlungen der Naturforsch. Ges. Basel*, 15, 9 (1903).

decimal place, at most, and that our knowledge of the density of the element copper is still less certain.

The above divergence is without doubt due to differences in the molecular configuration of the metal as a whole; for example, to the presence in varying amount of some form differing from the usual. The uncertainty due to this cause can be excluded by studying the after-effects of various factors on substances which crystallize well and without inclusions, and do not readily yield an amorphous or allotropic modification. Salts fulfil many of these conditions, and possess the further advantage that direct microscopic observation is a certain criterion of the actual homogeneity of the crystals. Such microscopic examination is necessary; for, as Retgers¹ showed, there are outstanding differences between the recorded values of the density of salts, which, while doubtless attributable in part to faulty experiment, result in the main from a lack of homogeneity of the material; that is, the differences found are due to the occurrence in the material of inclusions or of vacuoles in varying amount.

In view of these facts it was decided to test the after-effect of high pressures on the densities of some well defined crystallin substances. Since, however, one effect of very high pressures in some cases is a partial comminution of the material, it was necessary to ascertain if a change in density follows the reduction of a substance to powder, especially as contradictory statements with reference to this question appear in the literature.

In the present paper we propose to discuss the effect of various factors upon the density of solids. Much of the material presented has been derived from the somewhat scattered papers referred to in the text: our excuse for recapitulating it here is that many of the facts observed and the permissible conclusions to be drawn from them are apparently by no means generally known. Before proceeding to treat of the factors which may influence the real or apparent density of a solid, it is advisable to discuss the methods by means of which accurate determinations of the density of a solid may be made.

The Methods for the Determination of the Density of Solid Substances.

The more important of these are five in number: (1) the volumetric method; (2) by means of the volumenometer; (3) the flotation method; (4) by the method of Archimedes; (5) by means of the pycnometer.

(1) The volumetric method, as its name implies, consists in determining by direct measurement the volume of a definite weight of material; but, owing to the difficulty of obtaining sufficiently perfect geometrical forms, this method is not applicable where the highest accuracy is desired.

¹ J. W. Retgers, "Determination of the Specific Gravity of Salts Soluble in Water," *Z. physik. Chem.*, 3, 289 (1889).

(2) As regards the use of the volumenometer for determining the volume and hence the density of a substance, several types of instrument have been described, but none of them are accurate to better than 0.1%, and accordingly are insufficient for the purposes of the present investigation. We have constructed a modified type of the volumenometer described by A. Lo Surdo,¹ the accuracy of which, we had hoped, would be one part in 10,000. This accuracy we have so far been unable to attain; but until certain minor changes in the apparatus have been made, it will be impossible to make a definite report as to the precision attainable with this form of instrument.

(3) The flotation method possesses certain advantages, especially for the mineralogist, since a small fragment of material suffices, and the determination takes only a short time; on the other hand its applicability is limited by the lack of transparent liquids of sufficient density. In this method a heavy liquid is diluted with a lighter liquid until a small piece of the substance to be investigated remains suspended in the liquid. The density of the solid is then, of course, equal to that of the liquid, which is obtained by means of the Westphal balance or by any other appropriate method.²

(4) The method of Archimedes is well known. The most serious source of error is that caused by the action on the suspending wire of surface tension at the upper boundary of the liquid. This effect can be made very small, however, by using an extremely fine platinum wire previously coated with platinum black.³ For metals or other materials, which may be put in compact form, this is perhaps the most accurate method of density determination. With a weight of metal of 50 grams, the error should not exceed 2 or 3 parts in 100,000, if attention is paid to the temperature of the liquid.

(5) The principle of the pycnometer method is so well known that no description is required. It has at various times been proposed to use, as the pycnometer liquid, substances or solutions of high density in place of water in order to increase the accuracy of the results. Among the better known of the liquids which have been suggested are thallium ethylate, solutions of various borotungstates and a solution of the double iodide of mercury and potassium. It has however been pointed out⁴ that there is some important objection to the use of each of these as a

¹ *Sci. Abstr.*, 10, 2 (1907); from *Nuovo Cimento*, 12, 41 (1906).

² See for instance Merwin, *Am. J. Sci.*, 32, 425 (1911). Also Andreae (*Z. physik. Chem.*, 76, 491 (1911)), who by the use of a dilatometer is able to obtain results of a high order of accuracy.

³ Cf. Kohlrausch, *Praktische Physik*, 11 Aufl., p. 40.

⁴ Kahlbaum, Roth and Siedler, *Z. anorg. Chem.*, 29, 197-224 (1902). The reader, desirous of a full discussion of the accuracy of the various methods, is referred to this paper, and to a paper by J. W. Retgers, *Z. physik. Chem.*, 3, 289 (1889).

pycnometer liquid, particularly so when used with metals. For salts or any substances soluble in water where the use of water is precluded, xylene is a very suitable liquid. It possesses the advantage that air bubbles are very easily removed from it; and while its rate of evaporation is greater than that of water, no serious error from this source need be apprehended.

In general the pycnometer method (using water or xylene as the liquid) or the method of Archimedes is the most suitable for accurate work; we accordingly made use of these methods, the former for salts and other fragmentary material, the latter for metals. With the method of Archimedes, the temperature of the liquid was read to 0.1° in order to calculate the true density of the substance.

Determinations by the pycnometer method were made according to the procedure recommended by Day and Allen¹ except that the later measurements were made with a new type of pycnometer bottle, which was devised to obviate certain difficulties incident to the use (especially in the case of fine powders) of the usual type of bottle with tapered stopper. This type has been found so satisfactory in every respect that in all the later experiments we have used it altogether, for coarse as well as for fine powders.

An Improved Form of Pycnometer for the Density of Solid Substances.

The essential feature of this new form, which is illustrated in Fig. 1, is the plane ground joint, between stopper and bottle. The neck is made fairly thick, partly for the sake of strength, partly so as to minimize heat transfer when the bottle is held by the neck between the fingers. The two surfaces making up the ground joint should be *optically flat*, but not necessarily highly polished. Considerable care should therefore be exercised in grinding them properly, as the success or failure of the bottle depends upon the excellence of the joint. As a criterion of the quality of the joint, the stopper should be pressed forcibly on to the bottle with a slight rotary motion; if the grinding has been sufficiently well done, the bottle may be lifted by the stopper. In making this test the stopper should be dry, that is without grease or lubrication of any kind. Another requisit of success is that the pycnometer should be made in such a manner that no deep groove exists at A (see figure),² or indeed that there be no recess from which excess of water cannot readily be wiped away.

Pycnometers of this form have the following important advantages:

¹ Publication No. 31, Carnegie Institution of Washington, p. 55; *Am. J. Sci.*, [4] 19, 93 (1905); *Z. physik. Chem.*, 54, 1 (1905); or see W. F. Hillebrand, U. S. G. S. *Bulletin*, 422, p. 48.

² The bottles, which were made for us by the Emil Greiner Company, New York, were not entirely satisfactory as regards the grinding or freedom from grooves at the place indicated. However, by selecting two or three of the better ones, and grinding them further ourselves, we were able to obtain satisfactory results.

(1) The loss in weight by evaporation of the pyknometer liquid is negligible (for water it is of the order of 1 mg. in 24 hours). The pyknometer may therefore be allowed to stand in the balance case until temperature and moisture equilibrium is attained before it is weighed. (2) No grease or other lubricant is required on the joint; hence this obviates the uncertainty as to the weight of a variable, though small, amount of such grease. (3) Any small particles of grit or dirt which may accidentally lodge on the ground surfaces can be quickly and easily wiped off.



For these reasons this new type of pyknometer bottle gives considerably greater accuracy than the older forms; moreover, after very little practice its manipulation is quite as simple as with the older forms. After a few preliminary trials we were able to make successive fillings and weighings, both with water alone and with the sample plus water, which did not differ by more than 0.2 mg. This is illustrated by the following records, which are part of the results of an actual determination of the density of ground quartz which passed through a "200-mesh" sieve: weight of pyknometer filled with water at 25°, 29.6111 grams; after refilling, 29.6112; weight of pyknometer and quartz filled up with water at 25°, 34.1957 grams; after refilling, 34.1957; after standing 18 hours in balance case, 34.1953.

Fig. 1.—Improved form of pyknometer bottle.

In order to secure good results with this form of pyknometer it is highly important that attention be paid to the following details of manipulation: the loosely-stoppered bottle is immersed in a thermostat, the temperature of which should be constant to 0.01°, to such a depth that the water-level is 2 or 3 mm. below the ground joint, and is allowed to remain at least fifteen minutes. Enough distilled water at the temperature of the thermostat is then poured into the bottle to fill it to overflowing (less than 1 cc. will usually be required). The neck of the pyknometer is then held firmly with one hand while with the other the stopper is pushed on firmly with a sliding and slightly rotary motion. While the pressure is still being maintained¹ the pyknometer is removed from the thermostat and wiped dry around the stopper with a soft cloth. The bottle may then be grasped by the neck and the wiping completed. It is advisable as a precaution to pass the corner of a piece of filter paper around the stopper

¹ The purpose of this is to prevent the occurrence of a slight leak which may be caused by the apparent expansion of the liquid when the bottle is removed from the thermostat; this apparent expansion is due to the fact that under these circumstances the bottle cools slightly and contracts, while the temperature of the water remains practically unchanged.

and top of the pyknometer in order to remove any drops of water which may adhere. After standing ten minutes (or more) in the balance case, the pyknometer is ready to weigh.¹ Great care should be taken not to heat it by the hand, or otherwise, while it is being wiped and removed to the balance case. If these directions are followed the stopper will adhere firmly and not fall off even if the bottle is turned upside down.

The Correction of Densities to Vacuum.

To all determinations of density which purport to be accurate a correction for the buoyancy of the air must be applied. The error due to this cause can be eliminated by making separate corrections on each of the weights involved in the determination; but it is much easier, and less liable to error, to make the correction to vacuum in one operation. This may be done by means of the formula given below, or by reference to Table I; these results are applicable to any method in which density is measured by finding the weight of a certain liquid displaced by a given weight of the substance.

If s is the density of the substance as calculated from the uncorrected weights, S its true density, and L the true density of the liquid, then it can be shown that the vacuum correction to be applied to the uncorrected density, s , is $0.0012 (1 - s/L)$.²

The values of $0.0012 (1 - s/L)$ for densities up to 20 and for liquids of density 1 (water),³ 0.852 (xylene), and 13.55 (mercury) are given in Table I.

¹ It is, of course, advisable to use a counterpoise.

² Let s = density of substance calculated from uncorrected weights

S = true density of substance

L = true density of liquid

W_s = uncorrected weight of substance

W_l = uncorrected weight of liquid displaced by substance

Then by definition, $s = W_s/W_l$. (1)

Assuming D to be the density of the balance weights, $W_s(1 + 0.0012(1/S + 1/D))$ and $W_l(1 + 0.0012(1/L + 1/D))$ are the true weights of the substance and liquid respectively (assuming that the weighings are made under normal atmospheric corrections, so that the weight of 1 cc. of air is 0.0012 gram).

$$\text{Then the true density } S = \frac{W_s[1 + 0.0012(1/S + 1/D)]}{W_l[1 + 0.0012(1/L + 1/D)]} L.$$

But from (1) $W_s/W_l = s/L$. Substituting this in the above we obtain ultimately,

$$S = \frac{s + 0.0012}{L + 0.0012} L.$$

$$\text{Then the correction, } S - s = \frac{0.0012(L - s)}{L + 0.0012}. \quad (2)$$

Since L is always large as compared with 0.0012 the denominator of the above expression may be taken as equal to L , making

$$S - s = 0.0012 (1 - s/L).$$

³ A table of the corrections when using water is given in Ostwald's *Lehrbuch der Allgemeinen Chemie*, 2 Aufl., I, p. 285; but the sign of the correction as given there is wrong.

It is to be noted that when the density of the substance is greater than that of the liquid (as is usually the case) the true density is smaller than the apparent or uncorrected density. In other words, the correction is negative and is therefore to be subtracted from the apparent density. All of the original results given in this paper have been corrected in this manner for the buoyancy of the air.

TABLE I.—VACUUM CORRECTIONS FOR DENSITY (COR. $= 0.0012 (1 - s/L)$).

Density of substance (<i>s</i>).	Correction: density of liquid = 1 (H ₂ O).	Correction: density of liquid = 0.852 (xylene).	Correction: density of liquid = 13.55 (Hg).
0.8.....	+0.00024
0.9.....	+0.00012
1.....	0.0000	—0.0002	+0.0011
2.....	—0.0012	—0.0016	+0.0010
3.....	—0.0024	—0.0030	+0.0009
4.....	—0.0036	—0.0044	+0.0008
5.....	—0.0048	—0.0058	+0.0008
6.....	—0.0060	—0.0073	+0.0007
7.....	—0.0072	—0.0087	+0.0006
8.....	—0.0084	—0.0101	+0.0005
9.....	—0.0096	—0.0115	+0.0004
10.....	—0.0108	—0.0129	+0.0003
11.....	—0.0120	+0.0002
12.....	—0.0132	+0.0001
13.....	—0.0144	0.0000
14.....	—0.0156	0.0000
15.....	—0.0168	—0.0001
16.....	—0.0180	—0.0002
17.....	—0.0192	—0.0003
18.....	—0.0204	—0.0004
19...	—0.0216	—0.0005
20.....	—0.0228	—0.0006

Effect of Powdering a Solid upon its Density.

More than a century ago, Hassenfratz¹ published a paper in which he claims that by breaking up a piece of glass weighing about 50 grams into 2520 pieces,² a change in density ensued; but his experiments are in part discordant among themselves and are by no means accurate enough to decide the point at issue. His work may therefore be left out of account entirely; it has been mentioned here solely because its conclusions have been quoted occasionally.

The second paper, in point of time, dealing with this question, is one by G. Rose;³ it deserves mention if for no other reason because it has been widely cited and frequently by authors who apparently have not read through the original. Rose worked, on the one hand, with gold

¹ *Gilbert's Ann.*, 1, 369 (1799); *Ann. chim.* (Paris), No. 77, 188 (An 6).

² How this was accomplished without loss of material is not stated.

³ *Pogg. Ann.*, 73, 1 (1848).

and silver in the massive state, and with natural barite; on the other hand, with powders produced by precipitating these substances by chemical agency; and he found that in each case the density of the powder was the greater. He is careful to state, however, that this is no absolute proof that the density of a substance in a powdered condition is greater than that of a block of the same substance, since we cannot be sure of the complete identity of the substance in the two forms. Indeed, we now know that in very many cases the form of a substance when precipitated is different from that observed in nature or obtained by fusion. Rose's work, therefore, affords no information on the influence of the state of division of a substance on its specific gravity.

The Earl of Berkeley¹ has measured carefully the densities of two sizes of fragments of natural barium sulfate. For particles remaining on a sieve, the openings of which were 0.57 mm. on a side, he finds a density which averages 4.4702, while that of particles remaining on a sieve with 0.35 mm. openings averages 4.4700. The difference between the two densities is less than 0.005%—within the error of experiment. The difference between the sizes of the particles in the two cases, however, is so comparatively small that the evidence here adduced is insufficient to decide the point at issue.

It may be noted, in passing, that the above work of Rose has been cited² in support of an observation of Spring,³ according to which the amount of water required to fill the spaces of a given mass of sand is greater than would be expected if it were merely a phenomenon of occupying the air spaces. Spring's experimental work on this point is altogether insufficient to decide the question; his conclusion is based on the *assumption* that 26% of the total volume occupied by the sand consists of air spaces; even then the difference observed was only 0.8 cc., or but 0.25% of the total volume of the sand. In what follows it will be shown directly that this conclusion is false, since the density of solid substances, determined by the pycnometer, is found to be independent of the size of the particles, so long as these are strictly homogeneous, or even to show a slight decrease as the size of particle decreases; whereas, according to Spring's conclusion, the density should increase as the size of the particles decreases. A number of other early papers are cited by Spring in his first paper⁴ dealing with the change of densities of solids; these are all, however, concerned with changes of density produced by crystallization, vitrification, by tempering, hammering or annealing, and will be considered later.

¹ *J. Chem. Soc.*, 91, 60 (1907).

² Cameron and Bell, *Bull.* 30, Bureau of Soils, Department of Agriculture, p. 43 (1905).

³ *Mémoires Soc. Geol. Belg.*, 17, 13-33 (1903).

⁴ *Bull. Acad. Roy. Belg.*, [3] 6, 507 (1883).

Our experiments were made with quartz and potassium sulfate. The material was passed through a series of sieves, rated as 40, 60, 80, 100, 120, 150, and 200 meshes to the linear inch; the various samples were collected and dried at 200° for half an hour.¹ The earlier determinations of densities were made with the old style of pycnometer; the later ones with the new style described above. The liquids used were water and xylene,² the latter being used exclusively with the salts.

TABLE II.— d_4^{30} OF K_2SO_4 PARTICLES OF VARIOUS SIZES.

<i>Old Style Pycnometer.</i>	d_4^{30} .
Between 40 and 60 mesh.....	$\left\{ \begin{array}{l} 2.657_4 \\ 2.657_4 \end{array} \right.$
Between 100 and 120 mesh.....	2.656_3
Finer than 200 mesh.....	2.656_3

The results with potassium sulfate are brought together in Table II, which shows that the difference in density between the fine and the coarse powder is here scarcely greater than the error of experiment. A microscopical examination of the potassium sulfate showed that the crystals were free from inclusions or inhomogeneities of any kind.

For quartz the results shown in Table III were obtained. In this table each value of density represents a determination on a separate sample of material. It will be noted that with increasing fineness, the density increases by a small but definite amount reaching a maximum with particles 0.05 mm. in diameter (200 A) and then decreasing in the case of the very finest material (200 B).

This seemed difficult to account for until we discovered that, although a previous microscopical examination of one lot of ground quartz indicated that it was quite homogeneous, nevertheless the coarser particles of the lot from which our samples were taken contained a number of minute gaseous and solid inclusions; the finer particles (200 A), however, were almost entirely free from such inclusions. This fact accounts for the greater density of the 200 A. It is of interest to note in this connection that H. E. Merwin³ found the density of a number of fragments of clear quartz from different localities to be 2.6495 at 20° . Correcting the density to 25° ⁴ it becomes 2.6490—almost identical with the density of the 200 A material. This shows with great certainty that there is no difference in density between fragments of quartz 1 cm. in diameter and particles 0.05 mm. in diameter.

¹ Special experiments showed that the density of even the finest material was not appreciably affected by exposure to the air for 48 hours.

² For which $d_4^{30} = 0.85262$.

³ *Loc. cit.*

⁴ See *Smithsonian Physical Tables*, 215–216 (1904).

TABLE III.— d_4^{25} OF QUARTZ PARTICLES OF VARIOUS SIZES.*Old Style Pyknometer.*

Between 40 and 60 mesh.	Between 100 and 120 mesh.	Finer than 200 mesh.
2.648 ₇	2.646 ₆	2.649 ₂
2.645 ₆	...	2.648 ₁
2.645 ₆	...	2.646 ₈
2.647 ₁	...	2.647 ₁
2.646 ₆	...	2.648 ₈
2.647 ₃	...	2.649 ₈
...	...	2.648 ₃
...	...	2.646 ₃
Average....	2.646 ₆	2.648 ₀

New Style Pyknometer.

Between 40 and 60 mesh.	Between 80 and 100 mesh.	Finer than 200 mesh.	200 A. ¹	200 B. ¹
2.6471	2.6478	2.6488	2.6492	2.6483
2.6469	2.6476	2.6477	2.6486	2.6477
....	2.6483
....	2.6481
2.6470	2.6477	2.6482	2.6489	2.6480

With potassium chloride, the crystals of which contain a considerable number of holes, the density of the fine powder is considerably higher than that of the coarse material, as the following results indicate:

TABLE IV.— d_4^{30} OF KCl PARTICLES OF VARIOUS SIZES.*Old Style Pyknometer.*

	With sifted samples.	With ground and sifted samples.
Between 20 and 40 mesh.....	1.978 ₆	...
Between 80 and 100 mesh.....	1.982 ₉	...
Between 100 and 120 mesh.....	1.983 ₇	1.981 ₈
Between 150 and 200 mesh.....	1.984 ₁	1.982 ₈

It may be remarked that the density of the finest product was the same independently of whether it had been obtained by simply separating the fine crystals originally present or by grinding up some of the material of size between 20 and 40 mesh and subsequently sizing it between the 150- and 200-mesh sieves. These experiments suffice to show that when homogeneous material, free from cracks or holes, is powdered, the change of density thereby produced is but little greater than the error of the method employed. It may be noted, however, that the change, if real,

¹ A quantity of the powdered quartz which passed through a 200-mesh sieve was separated by a process of sedimentation into two nearly equal fractions. The coarser fraction (200 A), as seen under the microscope, consisted of sharp grains very uniform in size, namely about 0.05 mm. across. The finer material (200 B) was composed of particles, the size of which ranged from 0.02 mm. on down to the limit of vision of the microscope and probably beyond it.

is in both cases a decrease; and this may be a manifestation of the same phenomenon which is observed when metals are strained.¹

The After-Effect of Pressure on the Density of Solids.

For the experiments on the residual effect produced by very high hydrostatic pressures on the density of homogeneous crystals, we again used potassium sulfate, of size between 40 and 60 mesh. This size was chosen simply for the sake of convenience of manipulation; for from the preceding paragraphs it is evident that the effect of pressure does not depend upon the size of the crystal, so long as the material is strictly homogeneous.

The pressure bomb, of which a drawing to scale is given in Fig. 2, is of vanadium steel; it is 6 inches in length, 4 inches in internal diameter, with 1 inch diameter of bore. The plunger, of glass-hard steel, is a slip fit, but leak of oil past the plunger is prevented by the slice of soft rubber, *A*. Pressure was applied by means of a 500-ton hydraulic press, of which the platens are represented by *P P* in the figure. The figure also shows the arrangement by means of which the bomb centers itself. Without some such arrangement as this, it is next to impossible to obtain a rectilinear thrust parallel to the axis of the bomb; and, if this condition does not hold, leaks soon develop, and can be cured only by enlarging the bomb and by grinding a new and somewhat larger plunger to fit it.

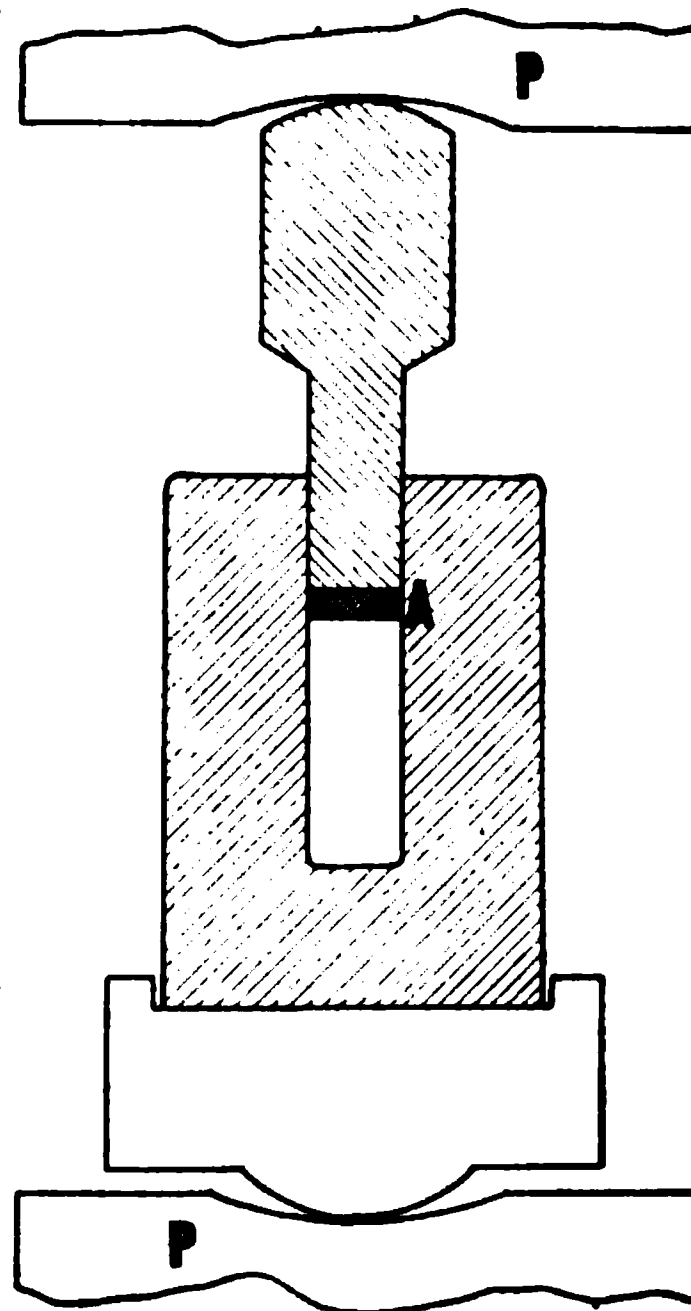


Fig. 2.—Shaded parts represent the bomb and plunger to scale; the other parts represent diagrammatically the press, platens *P P*, and the arrangement by means of which the bomb centers itself as pressure is applied to the plunger. *A* is the slice of rubber stopper.

The procedure was as follows: A quantity of about 10 grams of the substance was, in the earlier experiments, enclosed in a little bag of thin sheet rubber, the mouth of which was then tied tightly; but, as it was found impossible wholly to exclude the liquid used for compression, in the later experiments the substance was just placed within a copper tube, 1 cm. in diameter, closed at one end. The vessel containing the material was placed in the bomb and surrounded by paraffin oil (or by aqueous glycerol in some cases); the plunger was inserted, and the pressure was applied by means of a hydraulic press and continued for an hour or longer. The amount of pressure was calculated from the total com-

¹ Cf. *postea*.

pressive force exerted by the press, as measured on a hydrostatic gauge; the values given are only approximate, as no allowance was made for friction; they cannot, however, be in serious error. After the release of the pressure, the material was well washed with gasoline to remove the paraffin oil, and after heating for half an hour to 200° , its density was determined as described above. The results follow:

TABLE V.—AFTER-EFFECT OF HIGH PRESSURE ON THE DENSITY OF K_2SO_4 .

Density before compression.....	2.657 ₄
Density of one sample of same after 1 hour at 10,000 atmospheres.....	2.656 ₃
Density of a second sample of same after 1 hour at 15,000 atmospheres.....	2.655 ₈

Here again the differences are of the same magnitude as the error of experiment; again, however, it may be noted that the change, if it exists at all, is a decrease.

Spring¹ in his experiments on the after-effect of pressure on specific gravity of solids, compressed gradually in the dry state without the use of oil; the substance was subjected to pressure for a period of about three weeks, and after its density had been determined, to a second compression lasting some days. The amount of pressure was calculated to be some 20,000 atmospheres, but was probably considerably less, owing to the great friction incidental to such a method of compression. His experimental results on salts are contained in Table VI.

TABLE VI.—SPRING'S RESULTS ON THE AFTER-EFFECT OF PRESSURE ON THE DENSITY OF SALTS.

	Before compression.	After first compression.	After second compression.	Mean change produced by compression.
KCl.....	1.980	2.071	2.068	+0.090
KBr.....	2.505	2.704	2.700	+0.197
KI.....	3.012	3.110	3.112	+0.099
K_2SO_4	2.653	2.651	2.656	0.0
$(NH_4)_2SO_4$	1.773	1.750	1.760	—0.018
NH_4 alum.....	1.641	1.629	1.634	—0.009
K alum.....	1.758	1.756	1.750	—0.005
Cs alum.....	1.988	2.000	2.005	+0.014
Cr alum.....	1.828	1.823	...	—0.005
Tl alum.....	2.320	2.314	2.314	—0.006

This shows that the differences between the density after the first and that after the second compression are small and irregular; hence they are doubtless due to experimental error, which, to judge from the procedure employed, could easily have amounted to 0.005. The mean changes produced by compression are large and positive for the halides of potassium, just as one would expect from a microscopical examination, which shows that the crystals of all three substances are usually

¹ *Bull. Acad. Roy. Belg.*, [3] 6, 507 (1883).

not homogeneous, but contain small holes and flaws; with the other substances, excepting ammonium sulfate and cesium alum, the changes are hardly greater than the probable experimental error, while with potassium sulfate there was no change, in agreement with what we have found. On account of the anomalous change in density of ammonium sulfate found by Spring, we investigated the effect of hydrostatic pressure on the density of this substance; the procedure was identical with that described above except that prior to the determination of the density some of the samples were heated to 115° for half an hour; others, however, were dried in a vacuum desiccator and not heated at all. The results, presented in Table VII, of both sets of experiments are concordant, and show again that no after-effect has been produced by pressure.

TABLE VII.—INFLUENCE OF PRESSURE ON THE DENSITY OF $(\text{NH}_4)_2\text{SO}_4$.

(a) Samples heated to 115° before determination of the density.

Before compression.....	=1.765 ₈
After 2 hours at 12,000 atm.....	=1.767 ₁

(b) Samples unheated.

Before compression.....	=1.763 ₇
After 1 hour at 8,000 atm.....	=1.763 ₉

From the foregoing it is evident that the change of density observed after powdering a well-defined crystallin substance, or subjecting it to pressure, is in the direction of an increase only when the original substance contained cracks or holes; that is to say, an increased density is due entirely to accidental circumstances; with strictly homogeneous crystallin substances, on the other hand, the change of density is usually less than 0.001, and, if real, is in the direction of a decrease.

The Permanent Effect of Pressure on the Density of Metals.

That pressure may cause a *decrease* in the density of most metals has been known now for some time, though this phenomenon appears not to have attracted as much attention as it deserves in view of its bearing on the question of the constitution of metals. It was first shown for a number of metals by Kahlbaum, though it had been observed in isolated instances several times previous to him, but had not evoked much comment. H. Rose¹ observed that hammering silver caused a diminution in its density. Marchand and Scheerer found that pressed copper was, except for cast copper, the lightest, and further, that the density of bismuth decreased after compression.² Several investigators³ of the density of lead, who obtained results in part discordant, agree that its density is lessened by hammering and drawing, and sometimes by pressure.

¹ *Pogg. Ann.*, 73, 1 (1848).

² *Erdmann, J. prakt. Chem.*, 27, 209 (1842).

³ See F. Reich, *Pogg. Ann.*, 119, 541.

In 1862, C. O'Neil¹ found that sheet copper diminished in density by hammering, but regained the original value on subsequent annealing. Similar observations were made by A. Riche;² by alternately hammering and annealing blocks of steel or bronze, he found that though the hammering usually increased the density, the process of annealing caused a further increase in each case, instead of a decrease as might be expected. The next paper in point of time dealing with this subject is that of Spring,³ who determined the densities of seven metals before and after compression, using a method of experiment exactly similar to that described above in the case of the salts. Spring found that the second compression produced only very slight changes—decreases for two metals, lead and zinc, and increases for tin, bismuth, antimony, cadmium, and aluminium. The foregoing isolated instances would of themselves not deserve much confidence were they not confirmed by the very careful and trustworthy work of Kahlbaum and his collaborators.⁴ The latter distilled a number of metals *in vacuo*, subjected them for 11 hours to a pressure of 11,000 atmospheres, determined the densities, and in five cases out of seven subjected the metal for 1 hour to still higher pressures (Pb, Cd, Au to 12,000 atm.; Cu, Ag to 20,000 atm.); the densities were determined before and after each compression, with an uncertainty of probably not more than ± 0.0001 . His results are reproduced in Table VIII.

TABLE VIII.—INFLUENCE OF PRESSURE ON THE DENSITY OF METALS DISTILLED IN VACUO (KAHLBAUM AND COLLABORATORS).

	Original density. d .	After 11 hours at 11,000 atm. d' .	After 1 hour at higher pressure. d'' .	$d - d'$.	$d' - d''$.
Zn.....	6.9225	7.1272	...	0.2047
Sb.....	6.6178	6.6909	...	0.0731
Pb.....	11.3414	11.3457	11.3298	0.0043	—0.0159
Cd.....	8.6482	8.6477	8.6390	—0.0005	—0.0087
Au.....	18.8858	19.2653	19.2646	0.3795	—0.0007
Cu.....	8.9326	8.9377	8.9317	0.0051	—0.0060
Ag.....	10.4923	10.5034	10.4993	0.0111	—0.0041

From this it is evident that the first compression caused an increase, as might be expected, in the densities of all the metals with the exception of cadmium; but that the second application of pressure caused in every case a diminution, which was so great for three of the metals—lead, cadmium and copper—that the final density is actually lower than that originally observed, before any pressure had been applied.

Kahlbaum investigated very thoroughly the possible experimental

¹ *Fortschritte der Physik*, 18, 10.

² *Compt. rend.*, 69, 323 (1869).

³ *Bull. acad. roy. Belg.*, [3] 6, 537 (1883), to which we are indebted for some of the references above.

⁴ *Verhandl. Naturforsch. Ges. Basel*, 15, 9 (1903); in part in *Z. anorg. Chem.*, 29, 197 (1902).

errors, but was forced to the conclusion that the above variations represent real changes in the metals. To account for these changes he advances a somewhat fanciful *ad hoc* explanation on the basis of attractive and repulsive forces between the atoms, but makes no attempt to correlate these changes with other simultaneous changes in the metals. For instance, Kahlbaum remarks that his cylinders of metal had lost their polish and had suffered considerable deformation after compression, and especially after the second compression, but he had noticed these facts only incidentally. We now know that the oil (castor oil) used by Kahlbaum must have been nearly, if not altogether, solid at the higher pressures; consequently the metallic cylinder was then subjected to considerable differential compression, instead of to a simple hydrostatic pressure, as Kahlbaum apparently assumes was the case. This fact accounts for the deformations which he observed.

The more recent investigations instituted by Kahlbaum¹ on the changes in specific gravity of metals produced by deformation and by subsequent annealing confirm his previous results and those of Spring. He drew, or pressed, wires of various metals and alloys, measured their density, annealed them and again measured their density. The densities of wires which had been twisted a large number of times were also determined before and after annealing. A summary of his results is presented in Table IX. It will be noted that densities of the metals in the soft (annealed) state are greater in each case than the densities in the hard (drawn or twisted) state.

TABLE IX.—KAHLBAUM'S RESULTS ON THE DENSITIES OF WIRES.

Metal.	Original density of wire.	Density after annealing.	Difference.	Density after twisting.	Density after annealing.	Difference.
Au.....	19.2506	19.2602	0.0096	19.2220	19.2322	0.0102
Al.....	2.6995	2.7031	0.0036
Cd.....	8.6397	8.6434	0.0037
Ni.....	8.7599	8.8440	0.0841	8.8273	8.8412	0.0139
Cu-Al.....	8.2237	8.2377	0.0140
Pt-Ir.....	21.4766	21.4938	0.0172	21.3150	21.3309	0.0159
Pt, commercial.	21.4170	21.4320	0.0150	21.4112	21.4284	0.0172
Pt, pure.....	21.4336	21.4403	0.0067	21.3985	21.4319	0.0327
Wood's alloy ² ..	9.6661	9.6735	0.0074
Alloy IX ³	9.2837	9.2940	0.0103
Alloy VIII ⁴	9.7711	9.8223	0.0512

It remained for Spring⁵ to suggest the most probable explanation for

¹ Kahlbaum and Sturm, *Z. anorg. Chem.*, 46, 217 (1905).

² Composition: Bi 50%, Pb 25%, Cd 12.5%, Sn 12.5%.

³ Composition: Bi 47.75%, Pb 18.39%, Cd 13.31%, Sn 20.55%.

⁴ Composition: Bi 52%, Pb 32%, Sn 16%.

⁵ "The Effect of Compression in Diminishing the Density of Certain Substances and the Probable Cause of the Phenomenon." *Rec. trav. chim. Pays-Bas*, 23, 1 (1904); *J. chim. phys.*, 1, 593 (1903).

these changes in density: Namely, that a diminution in density occurs only in those cases in which a deformation has taken place. The gist of his argument is briefly as follows: That the substance, while it is being deformed, behaves as if it were partially liquid; that, when deformation has ceased, the substance may not wholly return to its original crystallin state, but partially remains in a state analogous to that of an under-cooled liquid, or, in other words, in an amorphous or glassy condition; and, since the density of the amorphous form is usually less than that of the corresponding crystallin form, the net effect would be a diminution in the observed density. If this reasoning be correct, it follows that metallic bismuth when deformed should show an increase of density; and Spring found this to be so. He fashioned wires of various metals by squeezing the metal through a hole 2 mm. in diameter, and made thin sheets by hammering; the densities were determined, the wires and sheets annealed and the densities again determined, with the following results:

TABLE X.—SPRING'S RESULTS ON THE CHANGE OF DENSITY OF METALS PRODUCED BY DEFORMATION.

	Density at 16° of			Mean difference.
	Wire.	Hammered sheet.	Annealed metal.	
Pb.....	11.3351	11.3348	11.3410	—0.0060
Sn.....	7.3011	7.3016	7.3137	—0.0123
Cd.....	8.6558	8.6603	8.6633	—0.005
Ag.....	10.2485	10.2531	10.2696	—0.019
Bi.....	9.8522	...	9.8354	+0.0168

These results are in agreement with those of Kahlbaum, except for the metals tin and bismuth, which the latter did not investigate. The anomalous behavior of bismuth as compared to that of the other metals is very important if true, since it furnishes strong evidence in support of Spring's theory.

Experiments with Bismuth.

Bismuth Cylinders.—In order to test this alleged behavior of bismuth, careful measurements were made of the densities of bismuth cylinders, first, after subjection to high pressures and again after annealing them. The bomb used for these experiments was of "type D" chrome-vanadium steel. The dimensions were: outside diameter 60 mm., diameter of bore 12 mm., length 80 mm. Pressure was applied directly to the metal by means of a hardened steel plunger. The whole sat beneath the press, and pressure was applied to the plunger as previously described on page 573. The cylinders were turned down to the proper diameter in a lathe; the diameter of cylinders I and II was practically the same as that of the hole in the bomb, while the diameter of cylinder III was 2 mm. less. The latter cylinder, therefore, when subjected to pressure was probably

first crushed to some extent and then welded together again at the higher pressures. As will be seen later, the density of this cylinder changed in a direction opposit to that of the other two. The pressure applied to each cylinder was about 15,000 atmospheres. Density was determined by the principle of Archimedes. The suspending wire was of platinum 0.1 mm. in diameter and was platinized according to the procedure of Kohlrausch. The cylinders were annealed by heating in a beaker filled with paraffin oil, and then slowly cooled to room temperature. After being wiped free from oil with a cloth, washed with "petroleum ether," and carefully dried, their densities were again determined. The results corrected to vacuum and to 25° follow:

TABLE XI.— d_4^{25} OF METALLIC BISMUTH, UNDER THE CONDITIONS STATED.

	Cylinder I. 33 g.	Cylinder II. 32 g.	Cylinder III. 41 g.
Density after pressing to 15,000 atm.	9.8012	9.7886	9.8001
After heating to 200° for 1 hour.	{ 9.8022 9.8020	9.7997
After heating to 240° for 2 hours.	9.8028	9.7898	9.7971

Since the act of forming wires from metals deforms them greatly, it was expected that bismuth wire might show a greater density change on annealing than the compressed cylinders. Accordingly a quantity of bismuth wire 1 mm. in diameter was made by pressing it out from a small bomb through a hole of that size. Wire was thereby produced which was initially flexible but broke upon being bent back and forth three or four times.

Density of Bismuth Wire.—About 20 grams of this wire were broken up into lengths of 6 or 8 cm., the pieces were bent into a circular shape and tied together with a weighed platinum wire. The density of the bundle of wires was then determined by the principle of Archimedes, special precautions being taken that no air bubbles remained in or on the bundle of wire. To make sure that this was the case, the wire was covered with air-free water in the beaker in which it was to be suspended. The beaker was then placed in a vacuum desiccator and the water caused to boil under reduced pressure for 10–15 minutes. Two determinations of the density of the wire gave 9.7693 and 9.7692 (corrected to vacuum and to 25°). After annealing at 230° for 2 hours the density was 9.7767 and 9.7768.

It will be seen that the density change upon annealing either the cylinders or the wire is in the same direction as with other metals, except in the case of cylinder III. The amount of change is small but undoubtedly greater than the error of experiment, which is probably not greater than ± 0.0005 . The increase of density observed with cylinder III we attribute to the inclusion of air at high pressure during the probable crushing mentioned above. A small amount of air included in this manner,

while having little effect on the density after compression, could expand during the process of annealing and thus give rise to the apparent decrease in density. This explanation may also account for the abnormal change in density observed by Spring, if indeed he made his density determinations on bismuth *before and after annealing*.¹

General Discussion of the Experimental Data.

Supposing these figures for the effect of pressure on the density of metals to be correct—and the magnitude of the differences surely greatly exceeds the probable experimental error—it may now be regarded as proved that deformation of a metal causes a change—usually a decrease—in its density.

Additional evidence in favor of this point of view is afforded by other papers. Gray and Mees² noticed that when hard drawn iron, brass, German silver, and pianoforte steel wires were stretched with increasing loads, a slight diminution in density set in when the elastic limit was reached. Grunmach³ stretched a bar of Siemens-Martin steel until it ruptured, and afterwards made a series of very careful density determinations throughout the length of the bar; he found that the density of both portions of the bar was constant and unchanged except at the broken ends, at which the density was less by 0.040 and 0.050, respectively.

From the foregoing examples, then, it is evident that deformation of metals is accompanied by a change—practically always a decrease—of density. This explanation conflicts with none of the available trustworthy experimental evidence on the densities of metals,⁴ and furthermore, it serves to correlate these facts with a number of phenomena observed by Beilby.⁵ Beilby's argument may be presented in his own words, it being premised that he uses the terms "crystallin" and "amorphous" to denote a homogeneous and a heterogeneous assemblage of molecules, respectively.

"Metals ordinarily occur in two distinct phases: the hardened or amor-

¹ For a discussion of this ambiguity cf. Kahlbaum and Sturm, *Z. anorg. Chem.*, 46, 303-5 (1905).

² *Phil. Mag.*, [5] 29, 355 (1890).

³ *Ann. Physik*, 67, 227 (1899).

⁴ The density data brought together in tables, *e. g.*, in Landolt-Börnstein-Meyerhoffer—cannot be made use of for such comparisons; the densities must be determined upon the *same* sample (1) when deformed and (2) after annealing, in order to obviate the effect of accidental circumstances—flaws, etc.—an effect which might easily exceed the effect sought.

⁵ For the present purpose, the best paper is in *Phil. Mag.*, [6] 8, 258-76 (1904), in which Beilby summarizes all his work up to that date. But see also *Proc. Roy. Soc. London*, (A) 72, 218, 226; 76, 462; 79, 463. The more important conclusions have been republished as reports, or abstracts, of lectures delivered by Beilby, in *Chem. News*, *British Association Reports*, and elsewhere.

phous, which will be referred to as the *A* phase, and the annealed or crystallin, which will be referred to as the *C* phase. The *A* phase is transferred into the *C* phase by the agency of heat, the *C* phase is transferred into the *A* phase by mechanically-produced flow. In the transformations $A \rightleftharpoons C$ there are two intermediate mobil phases *M* and *M'*; so that the transformation may be written $A \longrightarrow M' \longrightarrow C$ and $C \longrightarrow M \longrightarrow A$. The argument is based on evidence drawn from:

- (1) The distinct mechanical properties of the two phases *A* and *C*.
- (2) The microstructure of these and the evidence which it supplies of the existence of the mobil phases *M* and *M'*.
- (3) The (a) optical, (b) electrical, (c) thermochemical properties of the phases *A* and *C*.¹

Evidence was obtained in favor of these views with the malleable and ductil metals—gold, silver, platinum, copper and lead—and also with the brittle and crystallin metals—antimony and bismuth—the behavior of which falls perfectly in line with that of the former; further, with iron and nickel, which however possess other properties which occasionally render their behavior less plain and simple. The evidence presented in the case of silver, which occupies a fairly central position in respect to hardness and tensil strength, is here recapitulated, in order to show its character.

(1) The tensil strength of silver may be raised from under 10 tons per square inch to over 20 tons by rolling, hammering or wire-drawing. A strip of silver may be made quite hard and springy by hammering, but loses all its spring after heating to 260°.

(2) "The micro-structure of annealed silver, if the metal is in a sufficiently massive form, is always crystallin, and consists of grains built up of lamellae of similarly oriented units. In attenuated forms, like leaves or thin films, the structure is determined by surface tension, and has none of the characteristics of crystallin aggregation. The micro-structure of hardened silver is vitreous looking on the surface, and finely granular immediately below the surface. The forms assumed by surfaces and edges are rounded and smooth, and suggest the flow of a viscous liquid. When the glassy surface is carefully removed by a solvent, the granular structure underneath is more fully disclosed. By further action of the solvent the granular layer may be completely removed, disclosing the crystallin grains of the *C* phase more or less deformed or broken up. It seems probable that the granules which are thickly distributed through the vitreous layer are produced by the breaking down of the lamellae and the setting free of the units of which they are built up. The granules and their vitreous matrix always appear at surfaces of flow, the thickness

¹ Beilby, *Phil. Mag.*, [6] 8, 261 (1904).

of the layer being determined by the thoroughness of the flow at that particular place."¹

(3) (a) In beaten leaves or films, silver in its hardened state, is highly reflecting; by heating to 250–300° the leaf or film becomes transparent and loses much of its reflecting quality; but by flowing or burnishing the annealed leaf or film its opacity and reflecting power are restored.

(b) The electrical conductivity of a silver wire in the annealed state is 8–10% higher than that of the same wire in the hardened state. A thermo-junction composed of a hardened and an annealed wire of silver gave 0.17 microvolt per degree of difference between the hot and cold junctions; at 260° the electromotive force fell to zero, as the hardened wire then passes into the soft condition. Similar observations have been made by other observers, using various metals.²

(c) Berthelot³ found that the heat of solution in mercury of hammered silver was 2.03 cal., as compared with 0.47 cal. for annealed silver, and 0.10 cal. for crystals of electrolytic silver.

Thus by collecting the observations on the mechanical, optical, electrical and electrochemical properties of the hard and soft forms, it is seen that these all, without exception, support the view that there is a well-marked difference between the two states; further that they group themselves on either side of a transition temperature common to all; we are therefore justified in regarding these forms of a metal as distinct phases. The transformation from soft to hard cannot be brought about by reducing the temperature below the transition point, provided that no strains are set up thereby;⁴ but it is readily effected by mechanical means: for instance, in even the lightest and finest polishing this transformation or flow takes place to some extent at, and very near to the surface. When the metal is subjected to more drastic treatment, such as hammering or pressing, the effects penetrate to a greater and greater depth, and the transformation "takes place at all points where the strain reaches the stage at which mobility of the molecule is induced by the movement of one portion of substance against another." Thus "exceedingly thin layers of the A phase are formed throughout the whole mass of strained metal. Slipping is easy so long as fresh moving surfaces are forthcoming for the supply of the mobil phase; but when all the available crystalline phase has become encased in the unyielding amorphous phase, plasticity *under these particular stresses comes to an end.*"

¹ *Loc. cit.*, pp. 262–3.

² Magnus Maclean, *Proc. Roy. Soc. London*, (A) 64, 322; 66, 165. Spring, *J. chim. phys.*, 1, 600 (1903).

³ *Compt. rend.*, 132, 234–41 (1901).

⁴ Muir found that hardening by quenching results from the overstraining of the successive layers of material in a rod or mass of metal (*Proc. Roy. Soc. London*, (A) 71, 89).

"In the more easily flowed metals the surface film formed by polishing may vary from 1000–5000 $\mu\mu$ in thickness, while in the less easily flowed metals they may be 500 $\mu\mu$ or less. At surfaces which have moved over each other very slightly, films of only a comparatively few molecules might be formed."

Beilby was unable by any means to destroy all traces of the crystallin phase, even in the thinnest strips of gold or silver foil; indeed it has not been possible to produce more than a small percentage amount of the amorphous phase. Hence the properties of the latter can only be very imperfectly ascertained. All the evidence, however, tends to show that this amorphous phase is closely analogous to an undercooled melt, *i. e.*, it bears much the same relation to the crystallin metal as a silicate glass bears to the crystallin silicate.

On this view then we should expect as one of the results of the deformation, and consequent flow, of metals, a change of density in the same direction as that produced on melting; which agrees with the results actually found with the metals, bismuth excepted. Too much stress must not be laid on this exception, which may after all be only apparent. For though under ordinary conditions melted bismuth is denser than solid bismuth, it by no means follows that the melt produced at the pressures required to cause the metal to flow should be denser than the solid. As an illustration consider the behavior of water¹ with pressure: at pressures up to about 2200 atmospheres water is in equilibrium with ordinary ice (ice I), and the melting point decreases with increase of pressure up to that point; but at pressures greater than 2200 atmospheres, the melting curve rises again, and we have the water in equilibrium with other forms of ice, all of which are *denser* than the liquid water.

The plausibility of this view of the decrease of density of metals which have been deformed is increased by certain other considerations, which however, can only be referred to here. It is shown, namely, in another paper from this laboratory² that many of the properties of metals can be simply correlated if we assume that every *permanent* deformation of a crystallin solid is conditioned by, and consequent upon, a *real* melting; the whole of the solid does not, of course, melt, but only those portions of it which at any instant bear the brunt of the strain. On the basis of this assumption—the reasonableness of which is supported by a large variety of observations on the general behavior of metals—the possibility of accounting for changes of density following deformation is apparent; a plausible account of the mode of occurrence of these changes could easily be given, but at present it seems premature to do so.

¹ Tammann, *Krystallisieren und Schmelzen*, pp. 315–44. Bridgman, *Proc. Amer. Acad.*, 47, 441 (1912).

² Now in course of publication. A preliminary note was published in *J. Washington Acad. Sci.*, 1, 260 (1911).

Summary.

(1) With a new and improved form of pyknometer we have determined the density of salts and other substances with an accuracy of 3 or 4 units in the fourth decimal place, that is, within 0.02%. In many cases, however, such accuracy is unnecessary since the variations of density due to inhomogeneities of the material may be much greater than this.

(2) Powdering a crystallin substance does not change its density by an amount which we can detect with certainty, provided that the material is homogeneous and free from cracks and holes; but if the substance is not homogeneous, then, as might be expected, the fine powder is denser than the coarse particles.

(3) Neither does very high hydrostatic pressure produce any after-effect on the density of strictly homogeneous crystallin compounds.

(4) But if the pressure be not uniform, then the density of a metal which has been subjected to such compression—or has been deformed in any other way—usually increases first (owing presumably to the filling up of pores and cracks) and then decreases, sometimes even so as to reach a final density less than the original value. Subsequent annealing of the specimen causes a renewed increase of density. The direction of the change of density on compressing bismuth is, contrary to Spring's conclusion, the same as that for other metals, namely a decrease of density following upon deformation. The bearing of these results upon the question of the "flow" of metals is discussed: they are shown to be in harmony with the idea that the "flow"—or indeed any deformation—of a metal is a manifestation of a real melting produced by the unequal strains set up during the process.

(5) Finally it is important to emphasize the fact that the density of most substances is somewhat variable, owing to a lack of complete homogeneity of the material. In consequence of this, slight changes of density cannot be regarded as good evidence for the occurrence of any transformation or chemical reaction—whether produced by subjecting the system to compression or by other means.

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THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN CHLORIDE.

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In previous papers,¹ results have been given of a study of the electrical conductivity of solutions of the alcohols in liquid hydrogen bromide, and of the organic acids in liquid hydrogen chloride and bromide. These

¹ THIS JOURNAL, 29, 665 (1907); 29, 1416 (1907).

results showed that in these solvents the variation of the molecular conductivity with dilution over a considerable range of concentration was abnormal; as shown for other organic compounds in these solvents by Steele, McIntosh and Archibald,¹ in that the molecular conductivity increased with the concentration rather than with the dilution, as is the case with almost all aqueous solutions. As regards the solutions of the organic acids in hydrogen chloride, it was found that when the solutions examined became very dilute, the molecular conductivity-dilution curve changed its direction and continued to show the usual variation. In several cases these curves showed both maximum and minimum values for the molecular conductivity, notably for solutions of salicylic acid in the hydrogen chloride. Other cases of such variations in the molecular conductivity-dilution curve have been noted,² in particular by Franklin and Gibbs³ for solutions of silver nitrate in methyl amine and of various bromides in liquid sulfur dioxide: also by Schlesinger and Calvert⁴ for solutions of ammonia in formic acid. It was further found that in the case of the solutions of the organic acids, the hydrogen chloride formed much better conducting solutions than the hydrogen bromide.

It seemed well worth while to study some typical solutions of alcohols in liquid hydrogen chloride, to ascertain the nature of the variation of the molecular conductivity with dilution for solutions as dilute as could be examined. An attempt was also made to follow the conductivity of some of these solutions from pure hydrogen chloride through various concentrations of alcohol to pure alcohol. The results obtained are set forth below.

The preparation of the pure liquid hydrogen chloride and of the alcohols has been described in the papers cited above. The very small conductivity of the solvent, 0.02×10^{-6} , was strong evidence of its purity. Particular attention was paid to keeping water out of the pure liquid chloride solutions while the measurements were being made.

The method of measuring the resistance of the solutions was that of Kohlrausch, involving the use of the Wheatstone bridge, alternating current and telephone receiver. The conductivity vessels were of the "dip" variety, as previously described. Careful attention to the platinizing of the electrodes ensured a very satisfactory "minimum" in the telephone. Two sets of electrodes were used, one for solutions having a high, the other for solutions having a low resistance. The resistance capacities

¹ *Phil. Trans.*, (A) 205, 99 (1905).

² Kablukov, *Z. physik. Chem.*, 4, 429 (1889). Plotnikov, *J. Russ. Phys. Chem. Soc.*, 34, 466 (1902); 35, 794 (1903). Sakur, *Ber.*, 35, 1242 (1902). Kahlenburg and Ruhoff, *J. Phys. Chem.*, 1, 284 (1903). Walden, *Z. physik. Chem.*, 54, 131 (1906).

³ *THIS JOURNAL*, 29, 1389 (1907); *J. Phys. Chem.*, 15, 675 (1911).

⁴ *THIS JOURNAL*, 33, 1924 (1911).

of the cells were determined by measuring the conductivity of 0.01 and of 0.02 *N* solutions of potassium chloride.

Outside leak of current from one lead to the other due to the formation, on the outside of the conductivity vessel, of a film of aqueous solution of hydrochloric acid of very high conductivity, must be carefully guarded against, when working with dilute solutions in the hydrogen chloride.

The temperature of the bath of solid carbon dioxide and ether, in which the conductivity vessel was immersed, was kept at -89° by connecting the bath with a good water pump, and regulating the pressure over the carbon dioxide-ether mixture. The temperature was indicated by a pentane thermometer graduated to tenths of a degree.

The results obtained with the different alcohols are set forth in the tables below. We give in Table I the values found for the solutions actually measured and in Table II the values for the round concentrations. The dilutions are the number of liters containing one gram molecule of solute, the conductivity values are expressed in reciprocal ohms.

TABLE I.—SOLUTIONS IN LIQUID HYDROGEN CHLORIDE.

Methyl alcohol.		Ethyl alcohol.		Butyl alcohol.		Resorcinol.	
Dilu- tion.	Molecular conductivity.	Dilu- tion.	Molecular conductivity.	Dilu- tion.	Molecular conductivity.	Dilu- tion.	Molecular conductivity.
33.2	0.0528	48.8	0.0191	29.4	0.0238	12.64	2.930
15.19	0.0405	23.7	0.0182	11.1	0.0151	6.29	3.430
13.42	0.0395	12.19	0.0185	5.07	0.0178	4.09	3.770
8.31	0.0420	7.48	0.0200	3.21	0.0219	2.19	4.110
4.40	0.0528	4.66	0.0216	2.23	0.0244	1.222	4.270
2.91	0.0721	3.50	0.0268	1.53	0.0359	0.874	3.870
2.26	0.0981	2.58	0.0305	1.266	0.0638	0.681	3.610
1.608	0.1558	1.93	0.0378	0.944	0.0755	0.539	3.040
1.321	0.2282	1.48	0.0491	0.730	0.1262
1.056	0.3520	1.13	0.0798	0.574	0.2290
0.864	0.511	0.881	0.1405	0.336	0.442
0.649	0.832	0.713	0.267	0.272	0.470
0.694	1.190	0.591	0.361	0.2163	0.445
0.379	1.498	0.507	0.505	0.1613	0.332
0.273	1.622	0.423	0.645	0.1333	0.1173
0.201	1.587	0.332	0.799
0.156	1.457	0.263	0.902
0.130	1.199	0.173	1.155
....	0.156	1.045
....	0.131	0.878
....	0.120	0.803

As stated above, attempts were made to carry the measurements through the concentrated solutions of the alcohols in the liquid hydride, to pure alcohol. These attempts were, however, not entirely successful. The temperature coefficients of the conductivity for the concentrated solutions are so large that it is exceedingly difficult to obtain accurate measure-

ments. In the case of the methyl alcohol a compound separates out when about equal parts by weight of solute and solvent are present, and finally the whole mass solidifies. We hope soon to study these solutions from the other side, *viz.*, to measure the conductivity of the solutions of hydrogen chloride in alcohol, at temperatures corresponding to those obtaining in the above measurements.

Regarding these measurements of the concentrated solutions, we may say that on each side of the mixture which corresponds to the compound which separates out, the specific conductivity remains practically constant over a wide variation in the concentration, as the solution is diluted either with liquid hydrogen chloride or with alcohol. This is true of both the methyl and ethyl alcohol solutions. The maximum specific conductivity is about three times as great as that of 0.02 *N* potassium chloride at 18° C., *viz.*, about 0.00715 reciprocal ohms.

For the sake of comparison we give in Table II the values of the molecular conductivity for round concentrations, obtained from the curves given by the values in Table I.

TABLE II.—SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN CHLORIDE.
Molecular Conductivity.

Dilution.	Methyl alcohol.	Ethyl alcohol.	Butyl alcohol.	Resorcinol.
50.0	0.0191
35.0	0.0540	0.0185
30.0	0.0500
25.0	0.0452	0.0182
20.0	0.0420
15.0	0.0398	0.0183	2.852
10.0	0.0405	0.0190	0.0155	3.100
7.50	0.0435	0.0200	3.281
5.00	0.0502	0.0215	0.0180	3.670
2.50	0.0906	0.0271	0.0235	4.050
2.00	0.1260	0.0367	0.0275	4.140
1.50	0.1785	0.0479	0.0365	4.200
1.00	0.392	0.1055	0.0630	4.100
0.750	0.640	0.2060	0.1245	3.640
0.500	1.172	0.503	0.2920	2.910
0.250	1.624	0.955	0.465	...
0.150	1.470	1.048	0.261	...
0.1	1.060	0.704

The results for methyl, ethyl and butyl alcohol are shown graphically in Fig. 1, where, following the suggestion of Franklin, the logarithms of the dilutions are plotted as abscissas and the molecular conductivities as ordinates.

It may first be noted that here as in the case of the solutions of the alcohols in liquid hydrogen bromide, the lower the alcohol in the series the better conducting solution it forms; while the resorcinol gives solu-

tions which conduct better than those formed from the alcohols of the paraffin series, as was the case with the hydrogen bromide solutions.

1500

1000

500

Mol. Cond. ↑

Fig. 2

Before discussing these results further, we will give the values of the temperature coefficients of the conductivity found for the hydrogen chloride solutions. These are shown in Table III, expressed as percentage values of the conductivity at the lower temperature. The dilutions of the particular solutions are also shown, together with the temperatures between which the measurements were made.

TABLE III.—HYDROGEN CHLORIDE SOLUTIONS; TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

Dilution.	Temp. limits.	Methyl alcohol. Per cent	Ethyl alcohol. Per cent	Butyl alcohol. Per cent	Resorcinol. Per cent
137.0	—88.8 and —85.4	—1.33
6.29	—88.5 and —85.5	0.00
5.07	—89.3 and —85.8	5.23	..
4.68	—88.5 and —85.5	..	3.9
2.91	—89.0 and —86.0	1.21
1.06	—89.0 and —86.0	2.68
0.591	—88.0 and —85.0	..	4.0
0.574	—89.0 and —85.3	6.5	..
0.539	—89.0 and —85.0	+1.3

With regard to these temperature coefficients, we notice that the less the conducting power of the alcohol, the greater is the variation in the conductivity with temperature; while the temperature coefficient of the more dilute solution, and, therefore, of the poorer conducting solution of any one alcohol is less than that of the more concentrated. The solutions of the resorcinol are particularly interesting in this respect. Here we have rather good conducting solutions with negative temperature coefficients for the dilute solutions, and positive for the more concentrated. This behavior may be explained as follows: With rise of temperature presumably the fluidity will increase and the ionization will decrease. The first change will cause the conductivity to increase, the second will cause it to decrease. It seems as if for the concentrated solutions the effect of the change in viscosity overbalances that due to the change in ionization giving positive although small temperature coefficients; while for the dilute solutions the converse holds true, the effect due to the decrease in ionization overbalances the effect due to the change in fluidity, and we observe a negative temperature coefficient.

In like manner, by assuming a large change in the viscosity with change in temperature for the other solutions, we can explain the large temperature coefficients of conductivity; and this change will naturally be greater for the concentrated solutions than for the dilute, which is in accordance with the fact that the temperature coefficients are greater for the concentrated than for the dilute solutions. This point will be referred to again later.

Referring now to the values for the molecular conductivity in Table II, we note that for the more dilute solutions of methyl and ethyl alcohol the molecular conductivity varies with the dilution in the usual manner; *viz.*, it increases with the dilution as was observed in the case of the more dilute solutions of the organic acids in liquid hydrogen chloride. However, for dilutions below 15 liters per gram molecule, the molecular conductivity increases with the concentration, until it reaches a value about fifty times as great as its minimum value; it then decreases with the concentration quite rapidly for all the remaining measurements.

With regard to the curves shown in Fig. 1, they are very similar to the corresponding curve for solutions of salicylic acid in liquid hydrogen chloride; and in many respects to the curves obtained by Franklin for methylamine solutions of silver nitrate, and sulfur dioxide solutions of potassium bromide and iodide; except that for the solutions in the liquid hydrogen chloride, the increase of molecular conductivity with concentration is much more marked.

Lewis and Wheeler¹ have suggested that the increase of the molecular

¹ *Proc. Am. Acad.*, 41, 419.

conductivity with the concentration, in the case of weak ionizing solvents, may be due to autoionization of the solute. Franklin¹ explains his results with the methylamine and sulfur dioxide solutions in a similar way. He also explains the rise in the molecular conductivity shown for the first part of the curve—that for the concentrated solutions—by assuming that the increase in the conductivity with dilution, due to the decrease in the viscosity, is great enough for these concentrated solutions to overbalance the effect due to autoionization; while for the other end of the curve the increase in molecular conductivity with dilution is occasioned by the usual increase in ionization due to the solvent.

With regard to the solutions of the organic acids and alcohols in the liquid hydrides, similar explanations to those given by Franklin seem not unlikely to apply to the variation in the molecular conductivity at the two extreme ends of the curves, but for the greater part of the curve where the molecular conductivity is increasing rapidly with the concentration, some other explanation must be found, as it seems unlikely that in the case of a weak ionizing substance such as ethyl alcohol, autoionization would take place to a sufficient extent to cause the molecular conductivity to increase to fifty times its value between a dilution of 7.0 and 0.20 liters per gram molecule. The explanation offered by Steele, McIntosh and Archibald¹ for this abnormal behavior in the case of the solutions in the liquid halogen hydrides seems more likely to apply to the measurements recorded in this paper. This explanation assumes that there is a compound formed in solution between solvent and solute and that this compound which contains n molecules of solute is the electrolyte which is ionized. The concentration of the electrolyte is then proportional to the n th power of the concentration of the dissolved substance, while the molecular conductivity will be given by the expression kv^n rather than by kv ; where k is the specific conductivity and v the dilution of the solution in question.

The author has shown in previous papers, that when the molecular conductivity is computed according to this assumption for solutions of the alcohols and organic acids in the liquid halogen hydrides any one value of n for a certain solute is applicable only over a narrow range of dilution, indicating that the composition of the electrolyte varies with the concentration of the solution. The same variation seems to hold in the present instance. For the more dilute of the solutions examined the value of n must be 1 while over a considerable range the value $n = 4$ would seem very probable. Thus for methyl, ethyl and butyl alcohols the values of kv^4 for several dilutions are found in Table IV.

The same value of n applied to more dilute or more concentrated solutions would give almost impossible values. This is but additional evidence

¹ *Loc. cit.*

that a solution is a much more complicated system than we usually suppose.

TABLE IV.

Dilutions.	Methyl alcohol. kv^4 .	Ethyl alcohol. kv^4 .	Butyl alcohol. kv^4 .
2.50	1.395	0.421	0.363
2.00	1.008	0.293	0.220
1.50	0.599	0.161	0.123
1.00	0.392	0.105	0.063
0.75	0.268	0.085	0.052
0.50	0.146	0.062	0.036
0.25	0.025	0.015	0.007

It is interesting to compare the conductivity of the hydrogen bromide solutions of the alcohols with corresponding solutions in the hydrogen chloride. These are shown in Table V. The values for acetic acid in the two solvents are also included.

TABLE V.—MOLECULAR CONDUCTIVITY VALUES FOR HYDROGEN BROMIDE AND CHLORIDE SOLUTIONS.

Dil.	Hydrogen bromide solutions.				Hydrogen chloride solutions.			
	Methyl alcohol.	Ethyl alcohol.	Resorcinol.	Acetic acid.	Methyl alcohol.	Ethyl alcohol.	Resorcinol.	Acetic acid.
10.0	...	0.00048	0.076	0.0068	0.0405	0.019	3.10	0.236
5.0	0.00068	0.00050	0.127	0.0184	0.050	0.021	3.67	0.387
2.0	0.00166	0.00100	0.252	0.124	0.126	0.037	4.14	0.769
1.0	0.00925	0.00465	0.351	0.332	0.392	0.105	4.10	1.11
0.5	0.211	0.100	1.172	0.503	2.91	...
0.25	0.631	1.62	0.955

For the dilute solutions, we see that the hydrogen chloride solutions conduct between 50 and 100 times better than the solutions in hydrogen bromide, but as the concentration increases the conducting power of the different solutions becomes more nearly equal. This is due to the much greater increase in the molecular conductivity of the hydrogen bromide solutions with concentration.

Summary.

We may briefly summarize the foregoing results as follows:

(1) The conductivity of hydrogen chloride solutions of methyl, ethyl and butyl alcohols, and of resorcinol have been measured, and the temperature coefficients of the conductivity of these solutions have been determined at different concentrations.

(2) For the dilute solutions of the methyl, ethyl and butyl alcohols the molecular conductivity increases with the dilution, and this is also the case for the more concentrated solutions of all four solutes, but for a wide range of dilution the molecular conductivity increases with the concentration rather than with the dilution.

(3) The increase in the molecular conductivity with the dilution for

the concentrated solutions has been explained by assuming a considerable increase in the viscosity of the solution as the concentration increased with a corresponding decrease in the mobility of the ions.

(4) The decrease in the molecular conductivity with dilution over the greater part of the curve plotted in Fig. 1 is explained by assuming a complex electrolyte, containing n molecules of solute. The expression for the molecular conductivity is then kv^n rather than kv .

(5) The best conducting solution for the above solutes has a specific conductivity of 0.007 reciprocal ohms.

(6) The temperature coefficients for ethyl and butyl alcohols are very large and increase with the concentration. This is explained by assuming a large decrease in the viscosity of the solution with the temperature, this decrease being greater the more concentrated the solution. In the case of resorcinol the effect of the decrease in viscosity with temperature is great enough to change a negative temperature coefficient for a dilute solution, to a positive coefficient for a concentrated solution.

(7) The molecular conductivities of the above alcohols and of acetic acid in liquid hydrogen bromide and chloride are compared, the hydrogen chloride solutions being much the better conductors.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF FLUORINE.

[PRELIMINARY PAPER.]

BY D. J. MCADAM, JR., AND EDGAR F. SMITH.

Received March 18, 1911.

The present communication brings an account of experiments made to determine the atomic weight of fluorine by a new method. As the work has to be interrupted for a time it was concluded to offer such results as have been obtained.

A record of all previous work on the atomic weight of this element may be found in the third edition of F. W. Clarke's "A Recalculation of the Atomic Weights." Most determinations have been made by changing various fluorides into sulfates. This was the method pursued by Berzelius, Louget, Dumas, De Luca and Moissan, who used the fluorides of calcium, barium, lead, sodium and potassium. Their results vary from 18.85 to 19.14. The chief sources of error in the method are incomplete change of fluoride into sulfate, and loss of material due to the violent escape of hydrofluoric acid. Louget writes that, in spite of all precautions, there was always a slight loss of material. Naturally both these sources of error would lead to high values for the atomic weight.

Christensen¹ treated ammonium manganese fluoride, $(\text{NH}_4)_2\text{MnF}_6$,

¹ *J. prakt. Chem.*, [2] 35, 541.

with potassium iodide and hydrochloric acid, and titrated the liberated iodine. In this way he obtained four values for the ratio $(\text{NH}_4)_2\text{MnF}_6 : \text{I}$, the extreme variation being a little over 0.1% and the atomic weight 19.038. As Julius Mayer¹ has pointed out the iodometric method is subject to error, since some iodine is set free by the action of the hydrochloric acid on the potassium iodide. Moreover, Christensen gives no proof that his ammonium manganese fluoride did not contain other double fluorides of manganese.

Julius Mayer made five determinations of the ratio $\text{CaO} : \text{CaF}_2$. He prepared calcium oxide with great attention to removal of impurities and ignited to constant weight. He was unsuccessful in attempting to change calcium oxide to calcium fluoride by the direct treatment of the hydrated lime with hydrofluoric acid, as the material always gave an alkaline reaction when moistened. So he first treated the lime with hydrochloric acid, and then evaporated the chloride repeatedly with hydrofluoric acid to convert it into the fluoride. Special precautions were taken in ignition of the fluoride to constant weight. He has given no proof, however, of the completeness of the reaction, except to mention that the substance was neutral to litmus.

In this laboratory, we sought to change sodium chloride to fluoride by evaporation with hydrofluoric acid and, after seven evaporations, found much chloride remaining. Unless Mayer's term "mehrere" means much more than seven evaporations with hydrofluoric acid it is probable that his calcium fluoride contained traces of chloride, which would make his value for the atomic weight of fluorine, 19.035, somewhat too high.

It seemed desirable to try some other method. It was determined to change sodium fluoride into chloride with dry hydrochloric acid gas. It was hoped by this means to avoid the loss of material.

Preparation of Pure Material.

Water.—Ordinary distilled water was redistilled with addition of a little permanganate and alkali, a glass condenser being used. To the distillate a few drops of sulfuric acid were added and it was again distilled, using a quartz condenser. In most cases it was further redistilled from a Jena flask, employing a platinum condenser. It was either collected directly in platinum, or in flasks of Jena resistance glass, with covers ground on to the outside. No corks or rubber connections were used, and special care was taken to exclude dust.

Sodium Fluoride.—This was prepared from the acid fluoride, NaHF_2 , by heating the latter in a current of dry nitrogen or air. Since sodium fluoride is alkaline in reaction, it is evidently hydrolyzed by moisture; if heated in ordinary air, it is probable that some of the fluorine is replaced by hydroxyl.

¹ *Z. anorg. Chem.*, 36, 313 (1903).

The apparatus used in preparing the nitrogen consisted of a long, electrically heated Jena tube containing spirals of copper gauze. Through this tube, air saturated with ammonia was passed. It was then conducted through two U tubes containing dilute sulfuric acid to remove excess of ammonia, through a tower containing glass beads moistened with silver nitrate solution, through a bottle and tower containing concentrated sulfuric acid, through a tower containing small pieces of potassium hydroxide, through two towers containing boiled sulfuric acid, and finally through a long tube containing phosphorus pentoxide. The latter had been resublimed in a current of dry air directly into the tube in which it was to be used. All the apparatus, forward from the tube containing the copper gauze, was constructed of glass with ground joints. When a current of dry air was desired, ordinary air was forced through the same apparatus, after removal of the tube containing the gauze.

Sodium Hydrogen Fluoride (Sample A).—Very pure sodium carbonate was dissolved in pure water, the solution filtered and crystallization allowed to occur in platinum. The product was washed once by decantation and three times by centrifugal drainage. The centrifugal machine held two perforated platinum cones, and the average speed was 1500 revolutions per minute. The sodium carbonate was then considered to be pure enough for use in preparing acid sodium fluoride.

Commercial hydrofluoric acid was treated with one-fourth its equivalent of potassium fluoride, in order to form potassium silicofluoride from the silica present. A little potassium permanganate was also added in order to decompose any chloride that might be present. It was next distilled from a lead retort, with lead condenser, the retort being placed in a paraffin bath at 120° , since potassium silicofluoride is not decomposed at that temperature. The first fourth of the distillate, containing most of the chlorine, was rejected. It was then redistilled with addition of a little potassium fluoride and permanganate, rejecting the first portion as before. After four distillations, the last half of the distillate was found to be free from chlorine. It was then distilled three times from a platinum retort, rejecting the first and last portion each time. Traces of lead were thus completely removed.

From the last distillation, the liquid was collected in a platinum flask and was added to a portion of the sodium carbonate solution prepared as described above and contained in platinum dishes. At first the sparingly soluble sodium fluoride appeared, and being semi-gelatinous, it could not be centrifuged, but was allowed to settle and the supernatant liquid was decanted. To this sodium fluoride enough more hydrofluoric acid was added to produce the acid fluoride, NaHF_2 . This consists of small crystals, considerably more soluble in hot than in cold water, which can be centrifuged without difficulty. To test the purifying effect of this

scheme of crystallization, a portion of the crystals was mixed with sodium chloride and treated with silver nitrate, when a heavy precipitate appeared. But, after one recrystallization, only a slight precipitate occurred, while after two crystallizations, no test for chlorides was obtained.

The acid fluoride, after being centrifuged, was preserved in platinum dishes over solid potassium hydroxide, in desiccators thickly lined with paraffin. Every few days, the salt was stirred and all lumps were broken by gentle rubbing with a platinum spatula.

Sodium Hydrogen Fluoride (Sample B).—A portion of sample A was recrystallized from water containing a little hydrofluoric acid, centrifuged and preserved as in A.

Sodium Hydrogen Fluoride (Sample C).—A portion of sample B was again recrystallized and treated as before.

Balance and Weights.—The Troemner balance used in previous atomic weight work in this laboratory was again employed. Successive weighings of the same object agreed within 0.02 or 0.03 milligram.

The large weights were of brass, gold-plated, and the small weights were of platinum. They were of Class B, Bureau of Standards, and were carefully standardized.

The apparatus for carrying out the reaction is shown in Fig. 1; it was constructed entirely of platinum. A is a large tube drawn

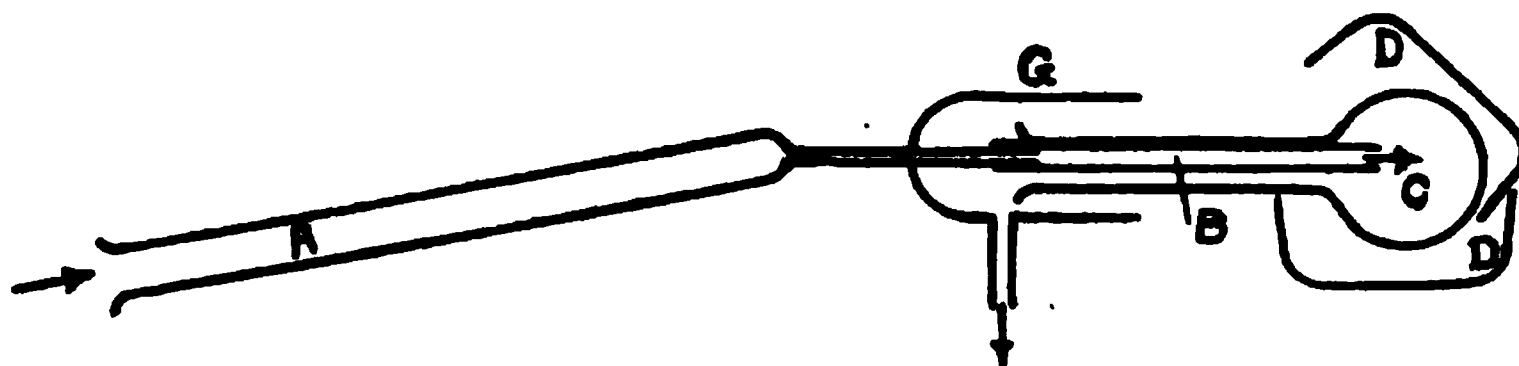


Fig. 1.

out to form a small tube at one end. B is the inner tube belonging to the flask C; it could be slipped over the small end of the tube A, and formed a support strong enough to hold the flask C. So the flask C, which was to contain the sodium fluoride, was supported entirely from the inside, and could be rotated so as to cause the sodium fluoride to roll around and expose fresh surface. D, D are platinum dishes, the upper being placed inside the lower and thus supported so as not to touch the flask C. These dishes were heated by Bunsen burners above and below, and the temperature of the air in this platinum oven could be regulated within ten degrees. G is a platinum tube, with small side tube through which the fumes were drawn by suction into an absorption apparatus. Fig. 2 shows the flask, with inner tube and stopper, in position for weighing. The stopper E fits it tightly enough to prevent diffusion, but not enough to make it air-tight.

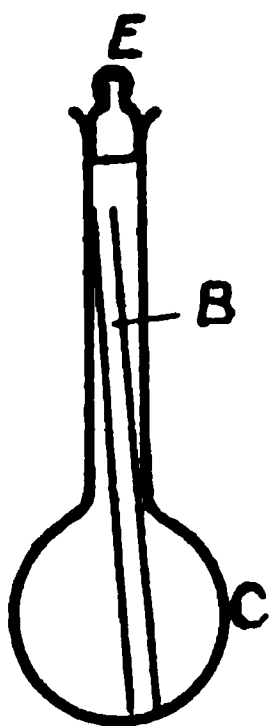


Fig. 2.

To the large end of the tube A, the tube from the nitrogen apparatus, or the tube from the hydrochloric acid generator, as the case might be, was adjusted by a ground glass joint.

The hydrochloric acid generator was constructed entirely of glass, with connections of ground glass or sealed by sulfuric acid. The gas was obtained by allowing sulfuric acid to drop into hydrochloric acid solution. It passed through a bottle of strong hydrochloric acid, and a bottle and tower containing sulfuric acid, and thence into tube A of the platinum apparatus. Enough acid was used in the apparatus to run an experiment continually for about forty hours.

Analytical Process.

The platinum flask, with inner tube and stopper in place, was weighed. Since sodium fluoride is slightly hygroscopic, it was necessary to weigh the flask filled with dry air. All weighings were by substitution of a counterpoise having nearly the same weight and surface as the flask. Platinum-tipped tongs were used in handling the flask. The acid sodium fluoride was now placed in the weighed flask and the apparatus was arranged as in the diagram.

After heating in a current of nitrogen, the flask and inner tube were removed and stoppered quickly to exclude moist air, and placed near the balance for several hours before weighing.

The experiments may now be described in the order in which they were performed.

Experiment (1).—Some sodium hydrogen fluoride (Sample A) was heated in the weighed flask for a period of four hours in a current of dry nitrogen at 325° , the nitrogen replaced by dry air and the flask restoppered and weighed.

Weight of NaF = 4.3281 grams; heated to $450-510^{\circ}$ for four hours. Weight of NaF = 4.3278 grams, and in dry air at 500° for two hours. Weight of NaF = 4.3274 grams.

It was thought that possibly the slight decrease in weight was due to hydrolysis, but later experiments with the vacuum desiccator showed the lower weight to be more nearly correct. So the weight of the sodium fluoride was taken as 4.3274 grams.

Dry hydrochloric acid gas was then passed over it, with frequent turning of the flask, the acid being finally displaced by dry air at about 400° . The duration of treatment with hydrochloric acid, with temperatures and weighings are given below and show the progress of the reaction. Its curve is similar to that of a reaction of the first order.

Time. Hours.	Temperature.	Weight. Grams.
8	370°	5.7749
9 ¹ / ₂	400°	5.9899
10 ¹ / ₂	440°	6.0019
10	460°	6.0088
10	460°	6.0131
11	470°	6.0167
10	450°	6.0176
10	460°	6.0186
34	460°	6.0204
35	460°	6.0213
24	460°	6.0211

The outside of the flask was rinsed with hydrochloric acid and then reheated in a current of dry air at 440° for an hour.

Weight of NaCl = 6.0209 grams.

The salt was again exposed to hydrochloric acid gas for 7 hours at 520°.

Weight of NaCl = 6.0208 grams.

With stopper loosely in place, the flask was held inclined in the blast flame until the contents could be seen, through the hot translucent platinum, to be entirely liquid:

Weight of NaCl = 6.02075 grams.

Constant weight was reached after heating through 180 hours. It was hoped that the reaction was complete; conditions seemed favorable, since the sodium fluoride was in a porous condition after the escape of hydrofluoric acid from the acid fluoride.

Assuming 58.46 as the molecular weight of sodium chloride, the molecular weight of sodium fluoride calculated from this experiment would be

$58.46 \times \frac{4.3274}{6.0208} = 42.0176$. If sodium is 23.000, the atomic weight of fluorine would be 19.0176.

Since no very delicate test for fluorides in the presence of chlorides had been worked out, the material was saved with the purpose of investigating it later.

Experiment (2).—This was a special experiment to learn how constant and definite a weight of sodium fluoride could be obtained by heating the acid fluoride in dry nitrogen or air.

4.85 grams of NaHF₂ (Sample C) were treated in the weighed platinum flask with dry nitrogen, in the cold, for an hour to remove traces of moisture, then for eight hours with a gradual rise of temperature from 350° to 520°. The nitrogen was then displaced by dry air.

Weight of NaF = 3.26104 grams.

It was then reheated in dry air at 450° to 500° for 4¹/₂ hours, stoppered quickly and placed in a vacuum desiccator. The air was quickly removed from the desiccator (and flask) and allowed to reenter after passing suc-

cessively through a tower containing pieces of potassium hydroxide and a tower containing glass beads moistened with boiled sulphuric acid. This process was used in all later weighings of the flask:

Weight of NaF = 3.26098 grams.

With the stopper of the flask loosely in place, the sodium fluoride was next fused in the blast flame; the material was seen to melt to a mobil liquid, its melting point being about 900° . While still hot it was transferred to the vacuum desiccator and treated as before.

Weight of NaF = 3.26098 grams.

It was fused again, cooled to dull redness, re-fused, and treated in the vacuum desiccator as before.

Weight of NaF = 3.26088 grams.

So the extreme variation of these four weighings is 0.00016, after two fusions. Some of the loss may be due to the sodium fluoride or even to the platinum itself.

This and the preceding experiment, therefore, prove that sodium fluoride may be brought to definite weight by the method of heating in a current of dry nitrogen or air, and that the weight is constant over a range of nearly 600° .

It also proves that the fluoride, when thus treated, contains no weighable amount of absorbed air.

Experiment (3).—Sodium hydrogen fluoride (Sample C) was treated with dry nitrogen in the cold for an hour, then with gradual rise of temperature from 300° to 500° for six hours with frequent turning. It was then treated in the vacuum desiccator as in previous experiments.

Weight of NaF = 3.3940 grams.

The salt was reheated in dry air at 500° for four hours:

Weight of NaF = 3.39398 grams.

The last weight was taken as correct, and the salt was heated in hydrochloric acid gas as in Experiment (1).

Time. Hours.	Temperature.	Weight. Grams.
56	450°	4.7211
29	450°	4.72194
39	450°	4.72232
35	450°	4.72244
41	450°	4.72292
<hr/>		
Total 200		

We abandoned the idea of obtaining constant weight by this method. Evidently some fluoride in the interior of each granule is not easily reached.

With stopper loose, the sodium chloride was now fused:

Weight of NaCl = 4.72260 grams.

It was thought that possibly the continued, small increase in weight was

due to minute particles of platinum being rubbed off from the entrance tube and falling into the flask; but, after rinsing, no increase in the weight of platinum was found, so the increase in weight must have been due to the chemical reaction alone.

The molecular weight of sodium fluoride calculated from this experiment would be $58.46 \times \frac{3.39398}{4.72260} = 42.0133$, and the atomic weight of fluorine would be 19.0133.

In future work we shall modify the scheme to ensure absolute removal of fluorine, the detection of which in small amount is at present very uncertain and extremely difficult. The treatment with dry hydrochloric acid gas will be followed by moistening with water and evaporating so as to expose fresh surface.

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A NEW METHOD FOR THE QUANTITATIVE ANALYSIS OF SOLUTIONS BY PRECISE THERMOMETRY.

[PRELIMINARY PAPER.]

BY THEODORE W. RICHARDS AND JOHN W. SHIPLEY.

Received March 16, 1912.

This paper describes concisely a new method of analyzing solutions which may be of very general application both in technical and in scientific work. The method depends upon noting the precise temperature at which the unknown solution attains exactly the same density as a given, previously calibrated solid float. This equality in density is marked by the familiar phenomenon, which we may call "floating equilibrium," where the wholly immersed solid neither rises nor sinks in the liquid. When, as is usual, the solution is denser than the solvent, the more concentrated the solution, the higher is the temperature necessary to reach floating equilibrium; hence, each concentration corresponds to a definite temperature, and after a few points on the almost linear curve connecting the two variables have been determined by means of known solutions, all the intervening ones are determinable by simply reading the thermometer at the points where floating equilibrium is attained. When the solution is less dense than the solvent, precisely the same method is used, except that the solution must be cooled instead of warmed to attain floating equilibrium, as the concentration increases. One should note that *differences* alone are the subject of study by this method; the exact density of none of the solutions need be known. The method is indeed more sensitive and accurate than any of the usual methods of determining the densities of liquids. The starting-point in each case should be the perfectly pure solvent, whose density, again, need not be

known; and the float is calibrated by solutions of known concentration.¹

The sensitiveness of the method is indicated by the following observation. A buoy-shaped or fish-shaped glass float, of not more than five cubic centimeters displacement, will distinctly change from floating to sinking when the temperature of the liquid is raised 0.001° , if just on the equilibrium point; and probably even a smaller temperature change would have an appreciable effect. This corresponds to a change of density of about 0.000001 in the case of most organic solvents, or about 0.000002 in aqueous solutions. If a 1% solution of a salt has a specific gravity of 1.01 compared with water at the same temperature, this degree of sensitiveness should enable one to estimate the amount of salt present to within 0.002% .

A mercury thermometer used for this purpose is best calibrated with all possible care; but if the bore is very uniform and the graduation is perfectly spaced, the degrees need not correspond to any recognized scale. Good results may be got with any good Beckmann thermometer. Platinum resistance thermometers or multiple thermopiles may be used with advantage by those familiar with very exact electrical measurements, if they possess apparatus from which stray electromotive forces are rigorously excluded; in this case ohms or millivolts may be plotted directly against concentrations without translation into centigrade degrees.

A thermostat capable of being easily adjusted at any needed temperature and of being kept there within 0.005° is required in order that the greatest accuracy may be attained. There is no great difficulty in accomplishing this; an Ostwald toluene-regulator of large capacity and large surface is arranged to make electrical contact with a movable wire in its capillary. This capillary is graduated, and the adjustment of the wire needed for any given temperature is easily found. The current thus regulated operates a relay for a stronger heating-current, or any other intermittent heating device.

The solution to be investigated is placed in a liter Erlenmeyer flask, immersed in the adequately stirred thermostat, and the float within the flask is viewed by reflection in a small inclined mirror kept beneath the water of the bath.

The float should be small and shaped, as has been said, like a buoy or fish, or very plump cigar. It should be made several months before it is used, if permanency in calibration is desired, so as to allow the attainment of constant volume after the internal upheaval due to heat. A recently made float may be used temporarily; but it must be recal-

¹ Since this work was finished, Andreae has published a method of determining the density of minerals which has some similarity in principle to the method herein described. The form of apparatus and method of application are different, however. *Z. phys. Chem.*, 76, 491 (1911).

brated with known solutions every few days. Approximate adjustment may be made by the addition of mercury or shot before sealing, and the final adjustment to any desired weight by adding glass to a short, thin, glass rod permanently attached to one end. Because the coefficient of expansion of the float as well as of the liquid enters into the effect, the results obtained with floats of different materials are not directly comparable. We have used common soft glass, Jena glass, and fused silica as the material for the float. The results given below were obtained with a float of common soft glass; but the best material is probably the standard thermometer glass, well known as Jena glass 59^{III}. We propose in the near future to publish results obtained with this glass.

The data of a single determination are recorded below in order to illustrate the method. In the first place, typical readings of a single setting may be given.

At 15.394° the float sank in the liquid.

At 15.390° the float rose in the liquid.

At 15.392° the float sank in the liquid.

At 15.390° the float rose in the liquid.

At 15.391° the float sank in the liquid.

Thus there was no question that the temperature could be fixed within 0.001°. It is not easy to attain the point where the float neither rises nor sinks, but this is not necessary; we contented ourselves usually with the narrowing of the range to within the small limit recorded above.

A series of measurements made by diluting 474.53 grams of alcohol of 98.99% purity by successive weighed additions of water, and taking the corresponding temperatures of floating equilibrium, is given below. The float used had been well seasoned, the temperatures were determined with the greatest care and referred to the international hydrogen standard, and all weights were reduced to the vacuum basis.

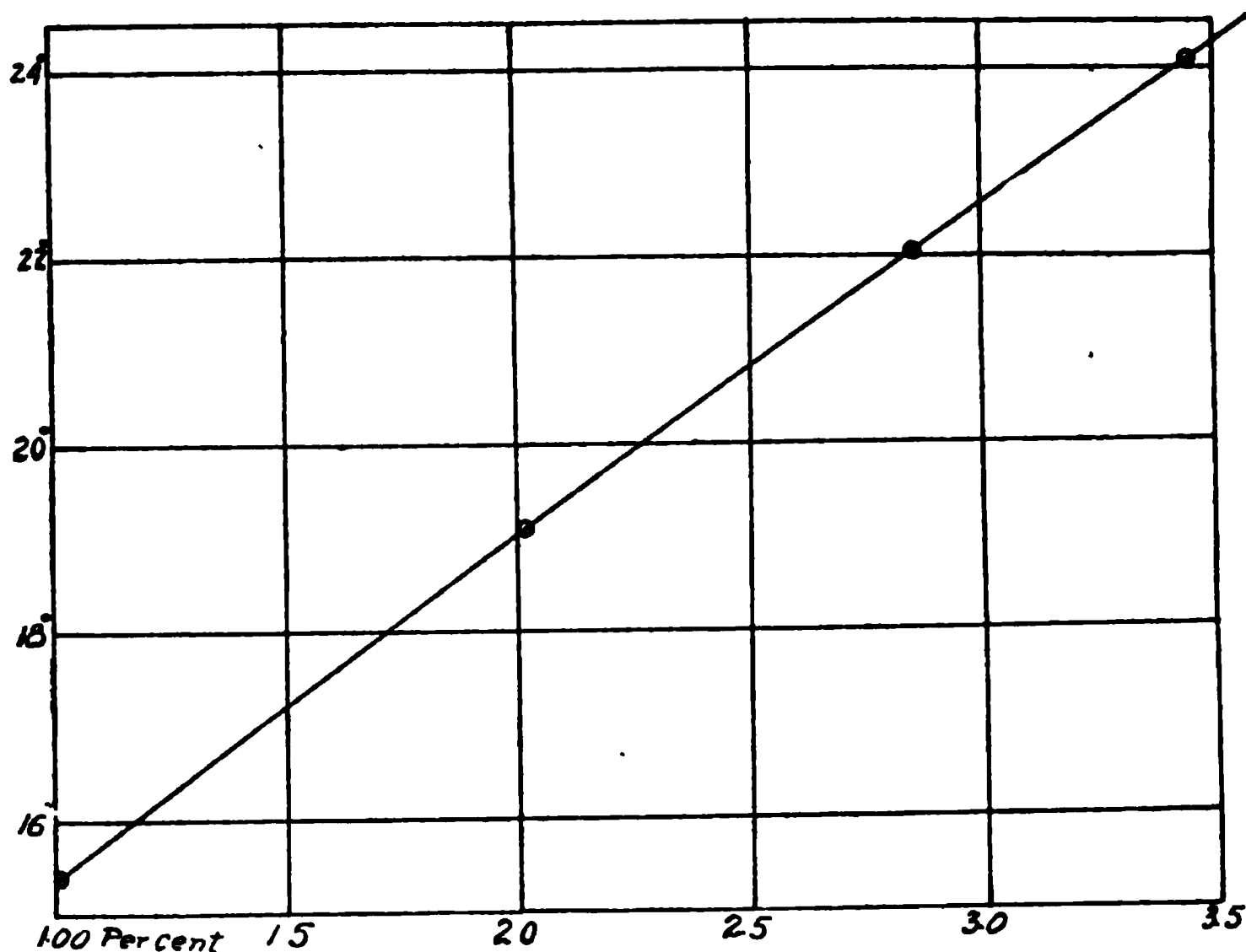
Water added (grams).	Per cent of water in alcoholic solution.	Temperature of floating equilibrium.
....	1.010	15.391°
4.8845	2.019	19.083°
4.1230	2.855	22.050°
2.9389	3.446	24.093°

Other series gave similar results, with curves exactly coincident when the start was made from the same concentration.

On plotting these results the following diagram is obtained, which must be drawn upon a very large scale to gain the full benefit of the accuracy of the method.

This curve may be used for the analysis by means of this float (or any other exactly similar float) of alcohol of any degree of purity between 99% and 96.5% (provided that water is the only impurity) as follows:

In one case, for example, a given specimen of alcohol was found to give floating equilibrium at 15.492° . Upon adding 9.550 grams of water to 375.77 grams of this alcohol, the floating equilibrium temperature became 24.251° . According to the curve, based upon the preceding table, these two solutions are found to contain 1.038 and 3.492% of water respectively. The difference between the two is 2.454. The



FLOATING EQUILIBRIUM TEMPERATURE AND CONCENTRATION.

Temperatures at which the float is in equilibrium with the solution are plotted in the direction of ordinates, and percentages of water in the diluted alcohol are plotted in the direction of abscissae. The curve is almost, but not quite, a straight line.

consistency of these results is seen from the fact that the difference as similarly calculated from the weight of water actually added is 2.453, assuming the first solution to contain 1.038% of water. The difference is only 0.001% of the total, or 0.04% of the added water. Many other similar experiments have been made with equal or even greater satisfaction, but they need not be recorded here.

Clearly the method is dependent upon the presence of only two components and demands for efficiency a decided difference between their densities. Where the densities are nearly alike and only trifling changes of volume occur on dissolving, the method is inapplicable.

For wide ranges of concentration one may use either several floats with different but overlapping ranges of operation, or else (less advantageously) a wider temperature range. It is evident also that the method may be used in a reverse fashion for standardizing thermometers by means

of known solutions. Thus, for instance, if a certain concentration of hydrochloric acid corresponds to a given temperature of floating equilibrium, and another equally definite concentration corresponds to another temperature, the difference between these temperatures can be fixed once for all by the mere titration of the two specimens of acid, and may be duplicated at any time with this float or one of the same density made from glass of the same coefficient of expansion. Such cases have been studied in detail and have been found to yield very satisfactory and interesting results. It is hoped before long to publish the somewhat voluminous data. For the present this preliminary paper will give an idea of the general problem and perhaps be of service.

It may perhaps be added that floats of this sort are of great service in preparing exact solutions (for example, in volumetric analysis) of predetermined density. In the present case, to cite a specific instance, alcohol of exactly 98.000% purity could have been made by setting the thermostat at 19.016° (read off from the curve) and adding water drop by drop to a purer alcohol until floating equilibrium was reached. For many years they have been used thus at Harvard to fix certain definite solutions at a fixed temperature.

Enough has been said in this paper to show that the method is one of considerable accuracy, and that it has a wide range of application to common problems of industrial as well as theoretical interest.

To recapitulate: it has been shown that the method of determining equality in density between a solid and a liquid by floating is applicable to a simple method of quantitative analysis, because the "floating equilibrium temperature" is an almost linear function of the concentration. Hence the reading of the temperature gives at once a determination of the concentration.

As this method is exceedingly sensitive, small changes in concentration may be detected with a degree of precision equaled by few other analytical processes. The process may be used either to determine concentrations by means of known temperature differences or else to determine temperature differences by means of known concentrations, when the relationships have been found once for all for any given substance. Thus it may be used not only to analyze solutions but also to calibrate thermometers, as well as to prepare exact solutions of any desired concentration. The coefficient of expansion of the solid float may also be determined with its help.

A more extended paper upon the subject in all its ramifications will be published in the near future. Much more work has already been done, and is almost ready to publish, and yet more is in prospect.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LEHIGH UNIVERSITY.]

THE SOLUBILITY OF SODIUM METAVANADATE.

BY D. J. MCADAM, JR., AND C. A. PIERLE.

Received March 21, 1912.

In making some experiments on the atomic weight of vanadium,¹ it was necessary for one of us to recrystallize sodium metavanadate quite often. In this work it was noticed that the crystals seemed to vary considerably in solubility and appearance.

Since we were not able to find anything definite on this subject in the literature of vanadium, it seemed worth while to investigate the solubility of sodium metavanadate, and to determine what hydrates occur in contact with the water solution.

Historical.—A. Ditte² says that $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ is obtained by allowing solutions to evaporate over sulfuric acid. He also says that he obtained crystals with $2\frac{1}{2}$, 3 and 4 H_2O by addition of alcohol to water solutions of sodium vanadate. Nothing was given about the solubility of these salts except the statement that they are slowly soluble in cold water and easily soluble in hot water.

In this laboratory in 1909, H. E. Maddock, at the suggestion of one of us, made a number of determinations of the solubility of sodium metavanadate. Most of the determinations were made at 25° , and the results varied from about $14\frac{1}{2}$ to $20\frac{1}{2}$ grams of vanadate to 100 grams of water. He also made one determination each at temperatures of 45° , 60° and 75° , getting values of 24.7, 33.6 and 40.8 grams respectively. The last two results agree very well with those of curve A as shown below. The explanation of the varying results at 25° is given later.

Preparation of Material.—Several samples of sodium metavanadate were prepared, but the method was in all cases practically the same, so only one preparation will be described.

Iron vanadate, the kind used in the preparation of ferrovanadium, was boiled with a strong solution of sodium carbonate or sodium hydroxide, filtered, and extracted several times with hot water containing sodium carbonate. The filtrate contained sodium vanadate, with the excess of alkali and some iron. It was acidified with sulfuric acid, which precipitated vanadic acid, leaving the iron and most of the sodium sulfate in solution; it was filtered with suction and washed repeatedly, but it was found impossible to wash out all the sulfate. As a means of removing this sulfate and also possible traces of phosphoric acid, the vanadic acid was then reduced to vanadyl oxalate by heating with oxalic acid. The equation is: $\text{V}_2\text{O}_5 + 3\text{H}_2\text{C}_2\text{O}_4 = 2\text{VO}(\text{C}_2\text{O}_4) + 3\text{H}_2\text{O} + 2\text{CO}_2$. Enough ammonium oxalate was now added to form the double salt $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{VO}$

¹ THIS JOURNAL, 32, 1603 (1910).

² *Compt. rend.*, 104, 1061.

(C_2O_4). This salt was recrystallized twice and filtered with suction. It now gave no test for sulfates. Ammonia was next added to a water solution of these crystals, and the brown precipitate was filtered and washed with dilute ammonia. The precipitate was then heated in platinum until no more ammonia was evolved. Part of the residue dissolved in sodium carbonate solution and the rest dissolved after fusion with sodium carbonate. Since the color showed that it had not been entirely reoxidized, a little sodium peroxide was added until the color of the solution disappeared. Both the sodium carbonate and sodium peroxide were of special purity according to the analysis of J. T. Baker.

The material was then treated with carbon dioxide to convert the excess of alkali into bicarbonate. It was next crystallized eight times in porcelain and three times in platinum, with drainage by suction, then four times in platinum with centrifugal drainage. During the final crystallizations it was protected from carbon dioxide by keeping it in a desiccator over potassium hydroxide. The water used in the crystallizations had been distilled from alkaline permanganate, and redistilled after addition of a trace of acid; a block tin or quartz condenser was used.

The sodium vanadate was now neutral, in hot or cold solution, to litmus, methyl orange, phenolphthalein and phenacetolin.

Apparatus and Method.—The thermostat was heated by gas, with a toluene regulator, and the water was kept well stirred. The temperature was usually constant to several hundredths of a degree, except at the higher temperatures, when it occasionally varied as much as 0.2° . The thermometer was standardized by the Bureau of Standards at Washington, and a correction was applied for the emergent stem.

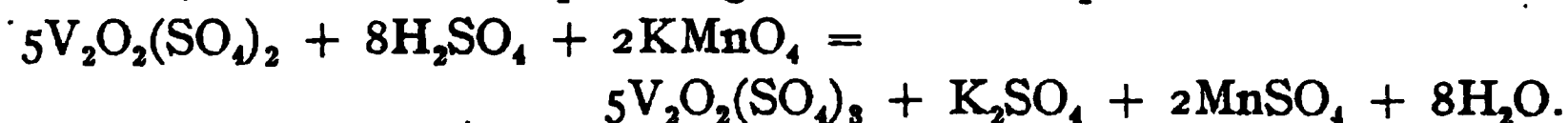
The solution and crystals were rotated in the thermostat in a hard glass tube closed by a well cleaned rubber stopper. When equilibrium had been reached, this tube was supported vertically in the thermostat until the crystals had settled, so that the supernatant liquid could be withdrawn.

A Landolt pipette was used for withdrawal of the solution. It was dried, weighed and kept in a vertical tube in the thermostat until ready for use. A filter of cleaned cotton wool was sometimes used in withdrawing the solutions.

After withdrawing the solution and wiping off the outside of the pipette, it was again weighed. The liquid was then washed out of the pipette and made up to a volume of 500 cc.; of this two portions of 100 cc. each were taken for analysis.

Analysis of the Solution.—The sodium vanadate was reduced to vanadyl sulfate by the action of sulfur dioxide in the presence of sulfuric acid. The excess of sulfur dioxide was then removed by boiling the

liquid in an atmosphere of carbon dioxide, and the liquid was titrated while hot, with standard permanganate. The equation is

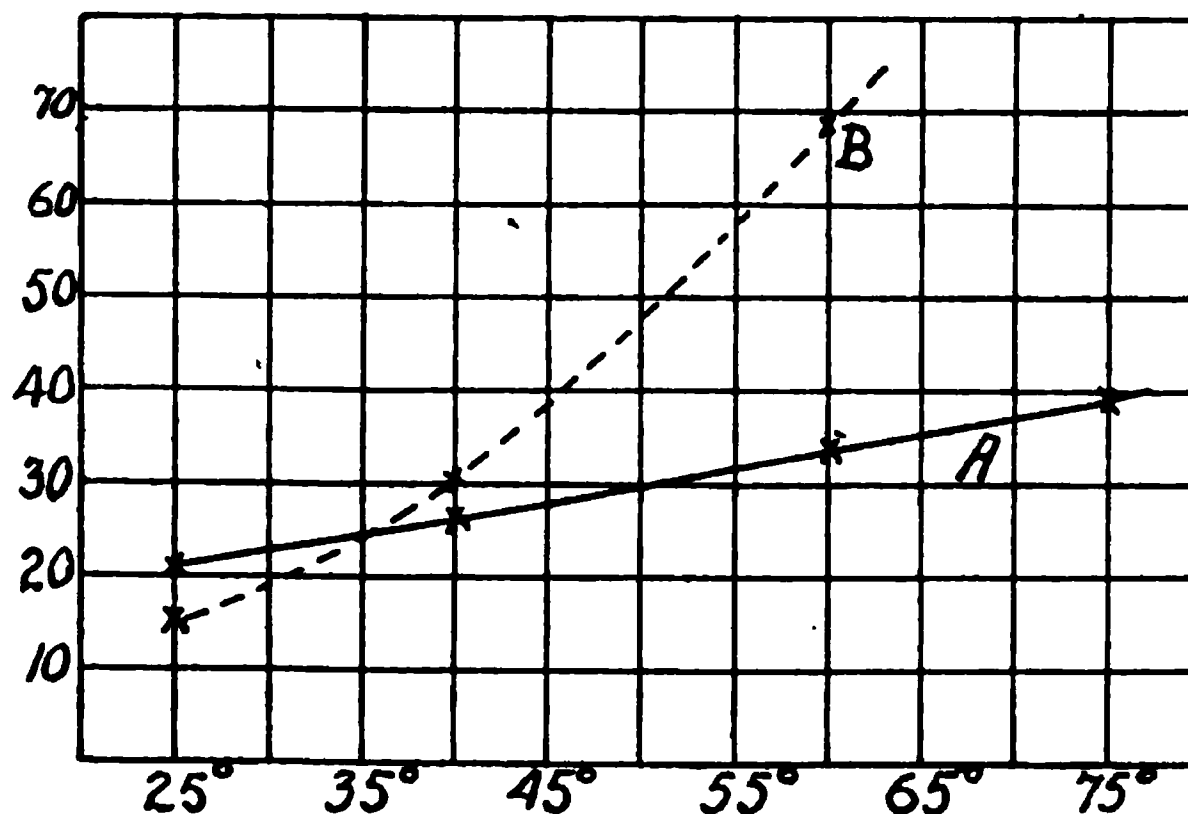


The permanganate solution was standardized approximately against oxalic acid and finally titrated against a known solution of fused sodium vanadate. The sulfur dioxide was prepared by the action of dilute sulfuric acid on sodium sulfite, and the carbon dioxide by the action of hydrochloric acid on marble; the gases were washed before entering the vanadate solution. Duplicate titrations made by this method agreed to within 0.05 cc.

Experiments and Results.—A number of preliminary trials were necessary before the proper conditions were secured. It was soon found that a long time was required for solutions of sodium vanadate to reach equilibrium, especially at the lower temperatures.

The following results were obtained with one sample of crystals: The values are expressed in grams of anhydrous vanadate to 100 grams of water. At 25°, after 24 hours in the thermostat, the solubility obtained was 21.30. After addition of fresh solid and a further run of 30 hours without change of temperature, the solubility was 21.27. After addition of water and a further agitation for 24 hours, the value obtained was 20.73. Saturation had evidently been reached, and the average value was 21.10.

Without addition of water or solid, the temperature was now raised to 40°, and the value obtained was 26.37; then more solid was added, and it was agitated for 27 hours more, giving a value of 26.07. The average value was 26.23. Another portion was then agitated at 60° for 24 hours, and gave a value of 32.97. The temperature was then raised to 75° and more solid was added. After six hours at this temperature, the value obtained was 38.83. These results are plotted in curve A.



Another sample of sodium vanadate gave quite different values, especially at the higher temperatures. The results are given below in tabular form. Sometimes fresh material was added for a new experiment and sometimes several determinations were made without allowing the thermostat to cool or adding new material. These results are plotted in curve B.

Temperature.	Hours.	Solubility.
25°	24	15.16
25	31	15.31
40	26	29.65
40	30	30.21
60	10	69.93
60	20	68.86
60	26	67.27
60	26	67.38

An attempt was made to get a value at 75° immediately after one of the experiments at 60°. At first, after raising the temperature to 75°, more solid went into solution, then suddenly more crystals began to form and the mass became nearly solid. It was then diluted with water and rotated again at 75°. The value obtained was 39.22; and, after eight hours more without addition of crystals or water, the value was 39.59. Another trial with the same material gave 38.15. The average was 38.99, which falls on curve A. So the solid phase had evidently changed to the less soluble modification.

The results, therefore, indicate that at least two different solid phases can exist in contact with water solutions, and that their solubility curves cross at about 35°. It is now clear why Maddock could not get consistent results at 25°. Evidently he was sometimes dealing with phase A, and sometimes with phase B, whose solubilities are 21.10 and 15.23 respectively. At higher temperatures his results agree fairly well with ours.

The next problem was to determine the composition of the two solid phases. This was quite difficult. The crystals were very small, those of phase A were so small that they could not be centrifuged effectively. Both kinds of crystals were anhydrous after exposure to the air, so it was hard to tell just when the mother liquor had been removed.

The first method tried was as follows:

Some of the crystals of phase B were centrifuged, weighed, fused and again weighed. The results were:

Wt. of crystals.	Wt. of anhydrous salt.
2.4550	1.9464
2.4620	1.8372

The loss of weight per hundred parts of anhydrous salt were therefore 26.13 and 34.01, with an average of 30.07. This corresponds to the formula $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$.

Since it was uncertain whether this loss represents water of crystallization alone, another method was now tried.

A small quantity of sodium chloride solution was added to the solution and crystals of sodium vanadate, and the material was rotated in the thermostat as in an ordinary solubility determination. The crystals were then freed as quickly as possible from the greater part of the solution, and analyses of the moist crystals and of the solution were made. The amount of sodium chloride found in the moist solid was assumed to be a measure of the amount of solution retained. The sodium chloride was determined by precipitating with silver nitrate in nitric acid solution and weighing the silver chloride. In another portion, the water was obtained by careful evaporation and fusion.

The results obtained by this method are given below. In each experiment, the first two horizontal columns give the results of actual analysis. In the third horizontal column, the values for NaVO_3 and H_2O have been calculated from the value for NaCl , so that the proportions are the same as in the first column. In the fourth horizontal column, the values were obtained by subtracting those of the third column from those of the second.

	Phase.	NaCl.	NaVO ₃ .	H ₂ O.	Solubility.	Formula.
Solution, 50°.....		0.1787	1.0538	3.6505	28.3	...
Moist crystals.....		0.0588	0.8497	1.3114
Retained solution...		0.0588	0.3467	1.2011
Dry crystals.....	B,	0.5030	0.1103	...	1.49H ₂ O
Solution, 50°.....		0.2233	1.5984	4.9585	32.21	...
Moist crystals.....		0.0450	3.7260	1.7311
Retained solution...		0.0450	0.3220	0.9992
Dry crystals.....	B,	3.4040	0.7319	...	1.46H ₂ O
Solution, 50°.....		0.1757	1.8413	5.0185	36.7	...
Moist crystals.....		0.0034	2.3523	0.6817
Retained solution...		0.0034	0.0356	0.0971
Dry crystals.....	B,	2.3167	0.5846	...	1.72H ₂ O
Solution, 35°.....		0.1242	1.2980	7.3859	17.6	...
Moist crystals.....		0.0489	1.9646	2.8911
Retained solution...		0.0489	0.5110	2.9079
Dry crystals.....	A,	1.4536	—0.0168	...	—0.078H ₂ O
Solution, 50°.....		0.1683	1.1374	5.0961	22.31	...
Moist crystals.....		0.0572	2.1868	1.7715
Retained solution...		0.0572	0.3806	1.7320
Dry crystals.....	A,	1.8062	0.0395	...	0.148H ₂ O

The solubility values, as given in the fifth vertical column, are of course lower than for pure sodium vanadate, and vary with the concentration of the sodium chloride. But it is evident from these figures that we had two different phases. To prove that the material used in the first three

experiments is really phase B, we made some solubility determinations at 50° with the pure substance. The results were 51.64, 52.21 and 52.20. By a reference to the curve it will be seen that these values are a little too high for curve B, but near enough to show that phase B had been obtained.

The values in the last vertical column are probably somewhat too low, since no allowance could be made for the effect of adsorption. In the third experiment the best result for phase B was probably obtained, since the moist crystals were centrifuged quickly before analysis and most of the mother liquor was thus removed. The value $\text{NaVO}_3 \cdot 1\frac{3}{4}\text{H}_2\text{O}$ obtained by this method, and the value $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ obtained by centrifuging alone, seem to us to show that phase B is $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$. From the last two experiments in the table, we conclude that the formula of phase A is NaVO_3 .

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 83.]

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.

PART V.—DETECTION OF THE ACIDIC CONSTITUENTS.¹

BY ARTHUR A. NOYES.

Received March 26, 1912.

Introduction.

This article forms a continuation of those previously published in THIS JOURNAL under the same main title.²

The purpose of the investigation here described was to work out a more systematic, generally applicable plan for detecting the acidic constituents of substances than those commonly employed. The attempt was also made to develop a series of tests for the various constituents of known and roughly equal sensitiveness. Moreover, the desirability of employing methods by which an approximate estimate of the quantities present could be formed was taken into consideration, as has been done throughout this system of analysis.

The execution of this research has been made possible through the effective aid rendered by Dr. W. C. Bray, Mr. R. D. Gale, and Dr. K. G. Falk, to all of whom I wish to express my great obligation. I am indebted to Dr. W. C. Bray also for invaluable assistance in the preparation of this article for publication.

General Discussion.

1. The usual method of testing for salts of the very volatil acids consists in liberating them by heating with a stronger acid and testing the

¹ Copyright 1912, by Arthur A. Noyes.

² THIS JOURNAL, 29, 137-205 (1907); 30, 481-563 (1908); 31, 611-637 (1909).

vapors with test papers or suspended drops of reagents. As this method gives little idea of the quantities present, it was considered inadmissible. Moreover, the usual separation of the acidic constituents from the heavier metallic elements by boiling with concentrated sodium carbonate solution is not satisfactory as a general procedure, since it fails to decompose most minerals and many other insoluble substances, since some metallic hydroxides (such as those of copper and aluminum) dissolve and separate from it upon neutralization, and since the necessity of decomposing the large quantity of sodium carbonate present in the solution makes certain tests impossible and others insufficiently delicate. A method free from these objections seemed to be the distillation of the substance with a strong non-volatile acid and collection of the distillate in water or a weak alkali solution; for this would serve to separate all the volatile acids from all the metallic elements, and would yield the former in a solution free from all other substances. A series of experiments showed in fact that a convenient and satisfactory procedure could be worked out by distilling the substance with phosphoric acid, which has been employed in quantitative analysis for a similar purpose.

This procedure must of course be supplemented by tests with fresh portions of the substance for the non-volatile acids, phosphoric and boric; for hydrofluoric acid, since this may be used up by action upon the glass; and for those acids which are decomposed by the distillation, such as thiosulfuric, hypochlorous, chloric, oxalic; but these last tests are necessary only in cases where their decomposition products have been found in the distillate.

2. The procedure finally adopted for the distillation consists in heating the solid substance in a flask with the pure 85% phosphoric acid of trade diluted with $2\frac{1}{2}$ times its volume of water and leading the vapors into a receiver containing barium hydroxide solution, until about half the water has distilled over. Then the solution in the receiver is replaced by pure water; and the distillation is continued till the phosphoric acid becomes nearly anhydrous.

By proceeding in this way the acids divide themselves into two main groups upon the basis of the readiness with which they pass over during the distillation. The first distillate contains the readily-volatile, slightly-ionized acids, namely carbonic acid, hydrosulfuric acid, sulfurous acid (from either sulfites or thiosulfates), hydrocyanic acid (from cyanides, ferro- or ferri-cyanides), nitrous acid, and free halogen (from oxyhalogen salts together with some reducing substance, or from halides together with some oxidizing substance). The second distillate contains the less volatile and largely ionized acids, namely, hydrochloric, hydrobromic, hydriodic, thiocyanic, nitric, and hydrofluoric acids; also chlorine from chlorates and carbonic acid from oxalates.

The separation of these two groups of acids is not a perfectly sharp one. A small quantity of some of those of the second group passes into the first distillate, but never in sufficient proportion to affect the tests for them in the second distillate. Of those of the first group, hydrosulfuric acid may occasionally be found wholly in the second distillate, namely, when it is present in difficultly soluble sulfides, some of which are decomposed only after the phosphoric acid has become concentrated. Some ferrocyanides are also so slowly acted upon that the hydrocyanic acid from them is found largely in the second distillate. When treating insoluble substances, it is therefore necessary to test for these two acids in both distillates. This involves little trouble, however, and the separation of the distillate into two parts has the great advantage that the tests for sulfurous and carbonic acids in the first distillate are not interfered with by the presence of sulfuric and phosphoric acids, which may pass over in small quantity into the second distillate.

An important proportion of the sulfuric acid and of the boric acid present does not pass over even into the second distillate, provided the distillation is stopped as soon as the phosphoric acid begins to fume. By adding finely divided copper and continuing the heating, sulfuric acid is reduced to sulfur dioxide, which passes over into a "third distillate," and can be there tested for in the usual way. It was found that one milligram of SO_4 could be readily detected in this way. It was thought that boric acid might also be distilled off from the phosphoric acid as methyl ester by adding methyl alcohol; but this was found not to be the case, apparently owing to the formation of a compound, boron phosphate (BPO_4),¹ with the phosphoric acid.

A disadvantage of this method of preparing the solution for the detection of the volatil acids is that certain acidic constituents in the substance, owing to decomposition, may give rise to the same product in the distillate; thus sulfites and thiosulphates both yield sulfurous acid; chlorates, hypochlorites, and chlorides (in presence of oxidizing substances), may all yield both chlorine and hydrochloric acid. When sulfurous acid or free halogen is found in the distillate, provision is therefore made (in Procedures 117-119) for testing an aqueous solution or aqueous extract of the original substance for sulfites and thiosulfates and for the oxyhalogen salts. This disadvantage, however, is compensated by the fact that the distillation shows whether special tests for these constituents are necessary, which, owing to their comparatively rare occurrence, is seldom the case.

3. The plan of analysis of the separate distillates may be seen in outline by reference to Tables XI and XII on the following pages. These outlines will not only serve to give the general reader a survey of the pro-

¹ Cf. Mylius and Meusser, *Ber.*, 37, 397 (1904).

cess, but they should be frequently referred to by any one employing the scheme for the first time, in order that the principles involved may be clear and the various procedures properly correlated.

The first distillate is collected in barium hydroxide solution, because loss of very volatile acids, like carbonic acid, is thereby avoided, and because the non-formation of a precipitate at once shows the absence of two acids of the group, carbonic and sulfurous acids. The detection of these two acids in the presence of each other and their separation from the other acids is complicated by the difficulty of filtering out their barium precipitates so as to yield a clear filtrate. To obviate this difficulty the plan was worked out in detail in the manner shown in Table XI and in Procedure 102. The presence or absence of another group of acids, namely, of nitrous acid and those acids yielding free halogens, is then shown by the addition of chloroform followed by that of potassium iodide.

Special tests for nitrite, sulfide, and cyanide are provided for. That employed for nitrite is the evolution of nitrogen by the action upon urea, which in acid solution is highly characteristic. Sulfide is tested for in acetic acid solution by the addition of a cadmium salt. Cyanide is detected in the usual way by its conversion into ferric ferrocyanide. Provision is also made for determining whether the hydrocyanic acid in the distillate originated from a readily decomposable cyanide or from a ferro- or ferricyanide; namely, by warming the original substance with a solution containing free carbonic acid (which displaces the hydrocyanic acid from simple and most complex cyanides, but not from the relatively stable ferro- and ferricyanides), and testing for hydrocyanic acid in the distillate.

4. In the analysis of the second distillate, silver nitrate and nitric acid are first added to determine the absence or presence of the acids that give a precipitate with silver salts; and then such special tests are applied as may still be necessary.

For the detection of chlorine in the presence of the other halogens, the method of distillation with sulfuric acid and bichromate was rejected, because of its lack of delicacy, because of the necessity of working with the dry substance, and because of the inconvenience which it involves. The method adopted is similar to that worked out by Jannasch¹ and Küster,² which is based on the successive liberation of the iodine and bromine by permanganate by producing the proper hydrogen-ion concentration in the solution and on their removal by boiling. This method was investigated in this laboratory by Dr. W. C. Bray and Mr. R. D. Gale, and was modified so as to make the tests for iodide and bromide more simple and delicate. The modification consisted in adjusting the acid concen-

¹ *Z. anorg. Chem.*, 1, 144, 248 (1892).

² See Crocogino, *Z. anorg. Chem.*, 24, 231 (1900). Böttger, *Qual. Anal.*, 387 (1908).

trations so that iodine and bromine were successively liberated at room temperature and in shaking them out into a solvent such as chloroform.¹

For the detection of nitric acid the usual ring test with ferrous sulfate and sulfuric acid was found not to be delicate enough to detect even five milligrams with certainty. The highly characteristic and delicate test based on its reduction to nitrous acid by boiling with ferrous sulfate and on the reaction of the nitrous acid in the distillate with potassium iodide was therefore adopted.

5. As stated above, supplementary tests must be made with the original substance in cases where sulfurous acid is found in the first distillate or where chlorine is found in either the first or second distillate, to determine the nature of the acidic constituents from which these substances originated. For these tests the solution is prepared by treating the substance either with water or (in order to free it from precipitable bases) with sodium carbonate solution, filtering, and acidifying slightly with acetic acid.

For the detection of sulfite and thiosulfate in this solution the method of Autenrieth and Windaus² is used, which is based on the fact that sulfite is precipitated by strontium nitrate, while thiosulfate is not. The latter constituent is then readily detected in the filtrate by the separation of sulfur which occurs on adding hydrochloric acid.

For the detection of hypochlorite, its characteristic power of oxidizing lead salts to brown lead dioxide is made use of. Chlorate is detected in the presence of hypochlorite or halides by reducing the former to chloride with sodium arsenite, precipitating all the halide present by silver nitrate, filtering, and adding sulfurous acid to the filtrate to reduce the chlorate to chloride.

Supplementary tests for certain non-volatile acidic constituents and for fluoride are also provided for. Phosphate, if not already detected in the analysis for the basic constituents, is tested for in nitric acid solution in the usual way with ammonium molybdate. The most satisfactory method of testing for boric acid, so as to afford at the same time a rough estimate of its quantity, seemed to be to heat the dry substance with methyl alcohol and sulfuric acid, to collect the distillate in a mixture of methyl alcohol and concentrated hydrochloric acid, and to add to it turmeric solution.³ Under these conditions an orange or red color results when borate is present. Fluoride is tested for by the Berzelius method of heating the dry substance in a tube with finely divided silica and acid potassium sulphate, and noting whether a deposit of silica forms on the cold part of the tube.

¹ Compare the volumetric method of titrating iodide described by Bray and MacKay, *THIS JOURNAL*, 32, 1193 (1910).

² *Z. anal. Chem.*, 37, 290 (1898). See Böttger, *Qual. Analyse*, 382 (1908).

³ A quantitative method based on this color reaction has been described by Hebrand (*Z. Nahr. und Genussm.*, 5, 56 (1902)).

Finally provision is made for analyzing silicates and other substances that are not decomposed in the phosphoric acid distillation, by fusing them with sodium carbonate and testing the aqueous extract for the acidic constituents that are likely to be present, namely for silicate, sulfate, phosphate, borate, fluoride, and chloride.

6. As has been done throughout this System of Analysis, the process has been described in such a way as to provide for the case that every constituent is present, it being left to the analyst to shorten it when certain constituents are proved absent in the course of the analysis or when information in regard to the character and source of the material excludes their presence. This method of presentation often makes the process seem longer than it is in practice; and this is especially true of this part which treats of the detection of the acidic constituents; first, because many of these are mutually exclusive, like hydrosulfuric, sulfurous, and nitrous acids, and free halogens; secondly, because the nature of the metallic element considered in connection with the solubility of the substance often makes the presence of certain of them impossible; and thirdly, because the nature of source of the substance, especially when it is a mineral or metallurgical product, excludes many of them.

7. Attention may finally be called to a simple modification of this plan for detecting the acidic constituents which it may be thought preferable to adopt as the general procedure, and which at any rate it may be advisable to employ in the analysis of certain classes of substances, for example of minerals not much acted upon by acids. The modification referred to consists in using the phosphoric acid distillation only for detecting the very volatil or readily decomposable acids (carbonic, hydrosulfuric, sulfurous, hydrocyanic, nitrous, and oxyhalogen acids), and in testing for the other acids (hydrochloric, hydrobromic, hydriodic, nitric, chloric, oxalic), which pass over (as such or as decomposition products) into the second phosphoric acid distillate, not in that distillate, but in an acid solution prepared directly from the original substance (or from a fusion of it with sodium carbonate). This is possible, since the tests for these last acidic constituents can all be made in acid solution, and since they are not interfered with by the presence of basic constituents. This modification might considerably simplify the formal description of the procedure and facilitate its comprehension by beginners. Attention is called to it also for the sake of emphasizing the ideas that the distillation procedure is especially valuable for detecting the readily volatil acids, and that, whether or not it is well to adopt it entirely, it affords a far more satisfactory method of testing for those acids than does the usual plan of liberating them in an open tube by warming with hydrochloric or concentrated sulfuric acid and examining the vapor as to its odor or color or as to its effect on test papers or suspended drops of liquids.

TABLE XI.—DETECTION OF THE ACIDIC CONSTITUENTS: DISTILLATION WITH PHOSPHORIC ACID AND ANALYSIS OF THE FIRST DISTILLATE. Distil 2 g. of the substance with dilute H_3PO_4 . Collect the first half of the distillate in $Ba(OH)_2$ solution and the second half in water. To the residue add Cu and distil again, collecting this third distillate in water (P. 101).

FIRST DISTILLATE.—Precipitate: BaCO ₃ , BaSO ₃ , S. Solution: Barium hypohalites (with halides), Ba(NO ₂) ₂ , BaS, Ba(CN) ₂ , SECOND AND THIRD DISTILLATES: see Table XII.					
To the whole mixture add HAc (acetic acid) (P. 101). Precipitate: BaSO ₃ , S. Solution: H ₂ CO ₃ , Cl ₂ , Br ₂ , I ₂ , HNO ₃ , H ₂ S, HCN. Treat portions of the unfiltered mixture as follows:					
Residue: S. (Shows SULFIDE or THIOSULFATE.)	Add HCl and filter (P. 102).		Introduce 1 cc. in- to an inverted tube filled with a solution of HCl and urea (P. 104).	Filter and add Cd(NO ₂) ₂ (P. 105). Precipitate: CdS. (Shows SULFIDE.)	Treat with NaOH, FeSO ₄ , FeCl ₃ ; boil, and add HCl (P. 106). Blue precipitate Fe ₄ (Fe(CN) ₆) ₃ . Shows CYANIDE.)
	Solution. Add Br ₂ .				
	Precipitate: BaSO ₄ ¹ .	Solution: H ₂ CO ₃ .	Gasevolved: N ₂ . (Shows NITRITE.)		
	Distil into Ba(OH) ₂ .				
	Precipitate: BaCO ₃ . (Shows CARBONATE.)				
	Add HAc and CHCl ₃ (P. 103). (Purple color shows IODINE.) (Orange color shows BROMINE.) Treat portions of the aqueous layer as follows:		Chloroform layer: I ₂ , Br ₂ , Cl ₂ . Shake with H ₂ SO ₄ .		
	If CHCl ₃ was colorless, add KI and CHCl ₃ .				
	Purple color- tion shows CHLORINE or NITRITE.				
	Water layer: HI, HBr, HCl. Test for separate halogens by P. 110.				

¹ Shows SULFITE or THIOSULFATE.

² The solution is subjected to this treatment only when the other tests have not led to definit conclusions as to the presence or absence of each of the three halogens.

TABLE XII.—DETECTION OF THE ACIDIC CONSTITUENTS: ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

Second distillate: HCl, HBr, HI, HSCN, H ₂ S, HCN, HNO ₃ . Treat separate portions as follows:					THIRD DISTILLATE:		
Add AgNO ₃ (P. 107). Precipitate: AgCl, AgBr, AgI, AgSCN, Ag ₂ S, AgCN.	If AgNO ₃ gives a precipitate, treat separate portions as follows:				Distil with H ₂ SO ₄ and FeSO ₄ (P. 111). Distillate: HNO ₃ . Add KI and CHCl ₃ . Purple color: (Shows NITRATE.)		
	¹ Add Cd(NO ₃) ₂ (P. 105). Precipitate: CdS. (Shows SULFIDE.)	¹ Test for CN (P. 106). Blue precipitate: Fe ₄ (Fe(CN) ₆) ₃ . (Shows FERRO- or FERRICYANIDE.)	Add FeCl ₃ and HNO ₃ (P. 108). Red color: Fe(SCN) ₃ . (Shows THIOCYANATE.)	Add CHCl ₃ (P. 109). CHCl ₃ layer: Water layer. Remove free halogen if present, by repeated shaking with CHCl ₃ ; then add NaAc, HAc, and KMnO ₄ , and extract with CHCl ₃ (P. 110).		Precipitate: BaSO ₄ . (Shows SULFATE.)	
				CHCl ₃ layer: I ₂ , Br ₂ , Cl ₂ . If colorless, add KI.			
			Purple color: I ₂ . (Shows CHLORINE.)	CHCl ₃ layer, Water layer. Add H ₂ SO ₄ and more KMnO ₄ and CHCl ₃ . purple: I ₂ . (Shows IODIDE.)			
				CHCl ₃ layer, Water layer. Boil orange: to expel Br ₂ , filter, add H ₂ SO ₄ , HNO ₃ and AgNO ₃ . Precipitate: AgCl. (Shows CHLORIDE.)			

¹ These tests are made only when the substance did not dissolve in the H₂PO₄ in the first part of the distillation.² Purple coloration shows IODINE, orange coloration, BROMINE.

TABLE XIII.—DETECTION OF THE ACIDIC CONSTITUENTS: SUPPLEMENTARY PROCEDURES.

Treat portions of the original substance as follows:

Distil with CH_3OH and H_2SO_4 (P. 113).	Heat with SiO_2 and KHSO_4 (P. 114).	Boil with HNO_3 , add $(\text{NH}_4)_2\text{MoO}_4$ (P. 115).	¹ Treat with water, HAc , and PbAc_2 , and heat (P. 117).	¹ Add dilute HNO_3 , Na_3AsO_3 , Na_2CO_3 solution and filter; to (to reduce hypochlorite), and filtrate add $\text{Sr}(\text{NO}_3)_2$ and HAc (P. 119).	² Fuse with Na_2CO_3 , extract with water, and filter (P. 116); acidify the filtrate, and test portions for chloride, sulfate, borate, fluoride, phosphate, and silicate.
Distillate: $\text{B}(\text{OCH}_3)_3$, Collect in CH_3OH and HCl , and add turmeric.	Gases evolved: SiF_4 and H_2O . Deposit on cold part of tube: $\text{SiO}_2\cdot\text{H}_2\text{O}$ (Shows FLUORIDE.)	Yellow precipitate: $(\text{NH}_4)_2\text{P}_2\text{O}_7\cdot 12\text{MoO}_3$ (Shows PHOSPHATE.)	Dark brown precipitate: PbO_2 (Shows HYPOCHLORITE.)	Precipitate: SrSO_4 , SrSO_3 . Treat with HCl and add BaCl_2 . Filtrate: SrSO_3 . Add HCl and heat. Precipitate: BaSO_4 . Filtrate: H_2SO_4 . Add Br_2 . Precipitate: BaSO_4 . (Shows THIOSULFATE.)	
Orange color (Shows BORATE.)			Precipitate: AgCl , etc. Reject. Filtrate: AgClO_3 . Add H_2SO_4 . Precipitate: AgCl . (Shows CHLORATE.)		

¹ These tests are made when free halogen was found in the first or second H_3PO_4 distillate.

² These tests are made when H_2SO_4 was found in the first H_3PO_4 distillate.

³ These tests are made only when the substance is not completely decomposed by hot concentrated acids.

Procedures and Notes.

Distillation with Phosphoric Acid.

Procedure 101.—Place 2 grams of the finely powdered substance and a few glass beads in a 100 cc. round bottomed Jena flask fitted with a rubber stopper through which pass a straight tube 20–30 cm. long leading to the bottom of the flask and a delivery tube. Fasten the flask in position at an angle of about 60° . Lead the end of the delivery tube through a two-hole stopper into 40 cc. of nearly saturated $\text{Ba}(\text{OH})_2$ solution contained in a 100 cc. flask supported in a large beaker of cold water. Boil in a small flask for about a minute a mixture of 25 cc. water and 10 cc. 85% H_3PO_4 (to expel any CO_2 present in it). Pour this mixture into the distilling flask with the aid of a small funnel connected with the long, straight tube. Heat the mixture to boiling, distil till about 10 cc. have passed over, and then remove the distillate. (White precipitate, presence of *carbonate* or some *sulfur-containing constituent*.)

Cool the distillate and make it slightly acid with acetic acid. (Complete or partial solution of the precipitate, presence of *carbonate*; residue (S or BaSO_3), presence of free *sulfur*, *sulfide*, *sulfite*, or *thiosulfate*)¹. If there is a residue, treat one-half of the mixture immediately by P. 102, and separate portions of the remainder by P. 103, 104, 105, and 106. If there is no residue, treat separate portions of the whole distillate by P. 103, 104, 105 and 106.

Introduce the end of the delivery tube of the distilling flask into another receiver containing 35 cc. water. Continue the distillation until the phosphoric acid becomes syrupy, boils more quietly, and begins to give off fine white fumes. Treat this distillate as directed in P. 107.

To the contents of the distilling flask, while still warm, add 5–10 grams of copper filings or turnings. Distil for 3–5 minutes longer, collecting the distillate in 15 cc. of water. Note the odor of the distillate, and treat it by P. 112.

Notes.—1. Since many of the tests for the different acids must be made in separate portions of the distillate, a larger sample is taken than for the analysis of the metallic elements, in order that detectable amounts may be present in these separate portions.

2. It is necessary to use a Jena glass flask, since one of ordinary glass is quickly destroyed by the action of hot, concentrated phosphoric acid. The boiling is sometimes violent, especially when much insoluble material is present. The addition of the glass beads serves to reduce the bumping; and placing the flask in a slightly inclined position prevents material from being thrown over into the distillate, which would lead to error in the subsequent tests. In any case in which it seems possible that some of the boiling liquid has been thrown over into the distillate, a small portion of the latter should be tested for phosphate by adding an equal volume of $(\text{NH}_4)_2\text{MoO}_4$ solution (see P. 115).

3. The point at which the second distillation should be stopped is fairly distinct.

¹ Such statements always refer to the presence of the constituent in the original substance, unless otherwise stated.

The chief indications of this point are that the phosphoric acid has become syrupy, that the boiling takes place more quietly, and that a hotter flame is required to maintain it. Also fine white fumes usually begin to appear, but they are not always plainly visible.

4. The saturated $\text{Ba}(\text{OH})_2$ solution in which the first distillate is collected is best prepared by adding 40 grams of the commercial crystallized hydrate to 500 cc. of boiling water, boiling 2 or 3 minutes, allowing the solution to cool and stand over night in a high, narrow vessel, and siphoning off the clear solution. The solution should, of course, be protected from the air as much as possible during the whole process. A mixture of BaCl_2 and NH_4OH can not well be substituted for the $\text{Ba}(\text{OH})_2$, since the ammonium acetate produced by the subsequent neutralization prevents the precipitation of a small quantity of BaCO_3 .

5. Phosphoric acid, which is ionized into H^+ and H_2PO_4^- to a moderate extent (about 27% in 0.1 molal solution), displaces almost completely from their salts (unless these are very difficultly soluble) the much less ionized acids, H_2CO_3 , HNO_3 , H_2S , HClO , HCN , HF , and H_3BO_3 , and also to a large extent the moderately ionized H_2SO_4 . Since all these acids, except HF and H_3BO_3 , volatilize readily out of aqueous solution, they pass over almost or quite completely into the first distillate, HClO in the presence of chloride giving Cl_2 . The largely ionized acids, HCl , HBr , HI , HSCN , HNO_3 , HClO_3 , $\text{H}_3\text{Fe}(\text{CN})_6$, and $\text{H}_4\text{Fe}(\text{CN})_6$, are not found in any considerable proportion in the first distillate, since they are displaced from their salts much less completely, and since in addition they are much less volatil. Of these the first five pass over unchanged and almost completely into the second distillate; for after the H_2PO_4 has become fairly concentrated, the acids are displaced to a greater extent and volatilize more readily in consequence of the higher temperature at which the mixture boils and the smaller proportion of water it contains. From the stronger H_2PO_4 solution HF also passes over in large quantity; but this is not true of H_3BO_3 and H_2SO_4 , which volatilize only in insignificant amounts even when the acid has become nearly anhydrous. The three acids, HClO_3 , $\text{H}_3\text{Fe}(\text{CN})_6$, and $\text{H}_4\text{Fe}(\text{CN})_6$, are not volatil as such, but are decomposed by the H_2PO_4 after it becomes fairly concentrated— HClO_3 with formation of Cl_2 and HCl , $\text{H}_3\text{Fe}(\text{CN})_6$ and $\text{H}_4\text{Fe}(\text{CN})_6$ with formation of free HCN . In regard to the acids that may be present in the two distillates, see also G. D., Section 2, and Tables XI and XII.

6. The barium salts of all the acids passing into the first distillate, except the carbonate and sulfite, remain in solution. Phosphoric acid, if thrown over mechanically, would, however, also give a precipitate. Sulfur, when present in the free state or when liberated from a polysulfide or thiosulfate, volatilizes with the steam, and gives a turbid appearance to the water condensed in the delivery tube and to the barium hydroxide solution, by which it is little acted on in the cold. Chlorine is converted by the barium hydroxide into barium chloride and hypochlorite; bromine, into bromide, hypobromite, and bromate; and iodine, mainly into iodate and iodide.

7. On acidifying the first distillate slightly with acetic acid, BaCO_3 dissolves, but BaSO_3 does not. This difference in behavior is due to the fact that hydrocarbonate-ion (HCO_3^-) is much less ionized than hydrosulfite-ion (HSO_3^-). Sulfur, if present, also remains undissolved. The addition of acetic acid causes the liberation almost at once of chlorine, bromine, or iodine from a mixture of hypochlorite and chloride, hypobromite and bromide, or iodate and iodide; but bromine is set free somewhat more slowly from a mixture of bromate and bromide.

8. A small precipitate obtained in this procedure (or in the following one) does not prove the presence of carbonate in the mixture unless the prescribed precautions are carefully observed—namely, the boiling of the original phosphoric acid solution, and avoiding the exposure to the air of the various solutions, especially that of barium

hydroxide. Even with these precautions, however, it is seldom possible to prevent the absorption of enough carbon dioxide to produce a slight turbidity in the barium hydroxide solution.

9. Upon boiling the H_2PO_4 with the copper, H_2SO_4 , if present, is reduced to H_2S ; and this passes over into the distillate in the form of SO_2 gas. Less than 1 mg. SO_2 can be detected by this process of distillation. The copper should be finely divided and should be added while the liquid is still warm, since on cooling it solidifies to a glassy mass, which consists of pyrophosphoric acid ($H_4P_2O_7$). The heating should be continued for 5-10 minutes; but, if much more prolonged, the contents of the flask change to a solid mass, owing to conversion of the pyro to metaphosphoric acid (HPO_3), which can afterwards be removed only with much difficulty.

10. With reference to the analysis of the first and second distillate, provided for in the subsequent procedures, certain facts are to be noted which in many cases greatly reduce the number of these special tests which it is necessary to make. In the first place, some of the acids are incompatible with each other, so that when certain ones are found, others need not be tested for: thus in the acidified distillate H_2S can not be present with H_2SO_4 , HNO_3 , or free halogen; HNO_3 and H_2SO_4 can not be associated with each other or with free halogen, etc. Secondly, the nature of the metallic elements taken in connection with the solubility of the substance often excludes certain acidic constituents; thus in a substance containing barium and soluble in water or very dilute acid, sulfate can not be present; in a water-soluble substance containing silver, none of the acids precipitated by silver nitrate can be present. Thirdly, the general character or known source of the substance may make many of the tests unnecessary; thus, it is useless to test a mineral for nitrite, sulfite, oxyhalogen salts, simple or complex cyanides, oxalate, or other organic salt. The analyst should, therefore, always consider these aspects of the problem, shortening the procedure in such ways as his knowledge makes possible.

Analysis of the First Distillate.

Procedure 102.—*Detection of Carbonate and Sulfur-containing Constituents.*—To one-half of the first distillate (P. 101), if there was a residue on adding acetic acid, add 1-2 cc. HCl (1.12). (Residue, presence of free sulfur, sulfide, or thiosulfate.) Filter, and add to the filtrate saturated bromine solution till the liquid becomes slightly yellow. (White precipitate, presence of sulfite or thiosulfate.) Transfer the mixture to a apparatus such as is used in P. 101, first filtering out the precipitate if it is large, distil for a minute or two, collecting the vapors in saturated $Ba(OH)_2$ solution. (White precipitate, presence of carbonate.) Acidify slightly with acetic acid. (Solution of the precipitate of carbonate.)

If H_2S is found in the distillate, treat a fresh portion of the original substance by P. 119, to determine whether it comes from a sulfite or thio-

1. See P. 101, N. 6-8. Since H_2SO_3 slowly oxidizes to H_2SO_4 in the air, it should be treated with HCl at once. If any H_2SO_4 has been formed in the distillate, it will be precipitated as $BaSO_4$ before the addition of Br_2 . Care must be taken to use enough Br_2 to complete the oxidation, since otherwise in the subsequent distillation O_2 will distil over and might be mistaken for carbonate.

2. If there is a large precipitate of BaSO_4 , it is filtered out, since otherwise it is difficult to avoid violent bumping during the distillation. Exposure to the air should, however, be avoided so far as possible, so that CO_2 may not be absorbed from it.

3. A residue of sulfur may arise from the presence in the substance of free sulfur, of a persulfide, of an ordinary sulfide together with some oxidizing substance, or of a thiosulfate.

Procedure 103.—*Detection of Nitrite and Constituents Yielding Free Halogen.*—To one-fourth of the first distillate (P. 101), or of what remains of it (P. 102), add 1–2 cc. 30% acetic acid and 2–3 cc. of chloroform, and shake vigorously. (Purple coloration of the chloroform, presence in the distillate of free *iodine*; yellow or orange coloration, of free *bromine*.)

If there is no coloration, pour about a third of the aqueous layer into a test tube, add 1 cc. chloroform and a few drops 1% KI solution, and let the mixture stand for 5 minutes, noting whether the color due to liberated iodine increases. (Purple color, presence in the distillate of *chlorine* or *nitrous acid*; no color, absence of *nitrite* in the substance.)

If there is a coloration after the addition of KI, test a 1 cc. portion of the first distillate (P. 101) for *nitrite* by P. 104.

If these tests show the absence of nitrite and the presence of free halogen, but do not warrant definite conclusions as to the presence or absence of each one of the three halogens, proceed as follows: Add 5 cc. HNO_3 (1.20) to the remaining two-thirds of the aqueous layer, separate the chloroform from it by means of a separating funnel, shake that layer a second and third time with 3 cc. of fresh chloroform, and separate the layers sharply again. Unite the three portions of chloroform, wash it once in the separating funnel by shaking it with about one-third its volume of HNO_3 (1.05), add the chloroform to an equal volume of H_2SO_4 solution in a separating funnel, shake, draw off and reject the chloroform layer, and test the aqueous layer for bromide and chloride by P. 110.

If free halogen is found present in the distillate, treat fresh portions of the original substance for hypochlorite by P. 117 and for chlorate by P. 118.

Notes.—1. For the reactions between the halogens and barium hydroxide and their reformation on acidifying with acetic acid, see P. 101, N. 6 and 7.

2. The free halogens distribute themselves between the chloroform and water phases. In the case of pure bromine or iodine the ratio of the concentration in the chloroform to that in the water layer is very large and is almost independent of the concentration. This is in accordance with the so-called distribution law, which requires that the ratio of the concentrations of a given molecular species, such as Br_2 or I_2 , in the two solvents be constant. When an iodide, like HI, is also present, the proportion of iodine extracted by the chloroform is greatly reduced, since the iodine in the aqueous layer is largely combined with the iodide in the form of the triiodide (HI_3); but it is still sufficient to make the color test a very delicate one.

3. The characteristic purple color given to chloroform is so delicate a test that even 0.05 mg. of iodine in the solution tested can be detected by this procedure. Bromine may be detected, but only in the absence of iodine, by the orange or yellow color

of the chloroform layer when not less than 0.5 mg. of bromine is present in the solution tested. (If a few drops of KI solution be added to one-third of the chloroform layer, the more intense color of the iodine liberated will enable a smaller quantity of bromine to be detected.) Chlorine gives no decided color to the chloroform, but like bromine causes liberation of iodine on the addition of KI. For extracting the halogens from aqueous solutions carbon tetrachloride or carbon disulfide may be used instead of chloroform; but carbon disulfide has the disadvantage of being highly inflammable.

4. Nitrous acid, like bromine or chlorine, liberates iodine from KI. The reaction is delicate enough to enable 0.1 mg. NO_2 to be detected in the solution tested. A peculiarity of this reaction is that the nitric oxide which is formed by it is rapidly re-oxidized by the oxygen of the air to nitrous acid, which then reacts with the iodide so that a continuous liberation of iodine results. Thus the nitrous acid acts as a catalyzer of the reaction between oxygen and HI. This progressive liberation of iodine is highly characteristic of nitrous acid, but renders it difficult to estimate the amount of it present. Since this behavior may not be a conclusive indication of nitrous acid, a fresh portion of the distillate is tested for it by P. 104.

5. If nitrous acid is found in the distillate, it shows the absence of free halogens, since nitrous acid is oxidized by chlorine or bromine very rapidly at room temperature and by iodine during the distillation with phosphoric acid.

6. An aqueous solution of chlorine contains a considerable proportion of HClO and HCl , sufficient to satisfy the equilibrium conditions of the reaction $\text{Cl}_2 + \text{H}_2\text{O} = \text{HClO} + \text{H}^+ + \text{Cl}^-$. Since the proportion present as Cl_2 decreases with decreasing hydrogen-ion concentration, and since only the Cl_2 dissolves in the chloroform, the quantity of chlorine extracted from a nitric acid solution must, in accordance with the distribution law, be much larger than from an acetic acid solution. In order, however, to extract small amounts of chlorine nearly completely it is necessary to add chloride as well as the acid.

7. When free halogen is detected by these tests it shows either that the halogen was present in the original substance in the free state, or (what is more common) that it was liberated during the distillation with phosphoric acid, from a halide by the action of some oxidizing substance, or from an oxyhalogen salt (such as a hypochlorite, chlorate, bromate, etc.), by spontaneous decomposition or by reaction with some reducing substances. When free halogen is found in the distillate, a portion of the original substance is therefore further tested (by P. 117 and 118) to determine from what source the halogen originated.

Procedure 104.—Detection of Nitrite.—If the results of P. 103 show that the first distillate may contain HNO_2 , determine its presence or absence as follows: Fill a weighing tube with a 20% solution of urea in HCl (P. 112), and invert it over a small dish containing more of the same solution. Introduce 1 cc. of the first distillate (P. 101) into the weighing tube by means of a small tube which has one end closed with a rubber nipple and the other end drawn out and bent so as to form a small U. Take care not to introduce an air bubble at the same time. (Formation of gas, presence of *nitrite*.)

Notes.—1. The reaction between urea and nitrous acid is



The N_2 is liberated in the form of minute bubbles which collect at the top of the tube. When much CO_2 is produced, it also separates as a gas; but a small quantity remains dissolved in the liquid. The amount of nitrite present may be estimated by making a comparative test with a known quantity of nitrite.

2. This procedure enables 0.1 mg. NO_2 in the 1 cc. of solution tested to be detected; but since such a small portion of the distillate is used a more delicate test may be desirable. If so, make a larger amount of the distillate slightly alkaline with NaOH , evaporate it to about 1 cc., acidify with a drop or two of HCl , and treat this solution as described in the procedure. In this process, before evaporating the solution, it is made alkaline so as to avoid loss of HNO_3 . The mixture is afterwards acidified so that carbonic acid may be expelled from it before it is introduced into the tube.

3. The halogens, chlorine, bromine, and iodine, when dissolved in alkali decompose urea with evolution of nitrogen, but they do not do so when dissolved in concentrated HCl . They do not therefore interfere with the test when carried out as above described.

4. Since all nitrites are at least moderately soluble in water, this test may be made with an aqueous solution or aqueous extract of the original substance. The test should be so made when the nature of the substances present makes it possible that nitrous acid may have been completely decomposed during the distillation with H_3PO_4 .

Procedure 105.—Detection of Sulfide.—To one-half of what still remains of the first distillate (P. 101), add 2 cc. 10% $\text{Cd}(\text{NO}_3)_2$ solution. (Yellow precipitate, presence of *sulfide*.)

Notes.—1. The presence of H_2S is usually detected in the distillate by its odor; but the precipitation of CdS from a weakly acid solution has the advantage of enabling the amount of sulfide to be approximately estimated. When this test is applied to a strongly acid solution from any other source, sodium acetate should also be added.

2. A negative test for H_2S in the first distillate does not prove the absence of sulfide in the original substance, unless the latter has dissolved completely in the dilute H_3PO_4 ; for some difficultly soluble sulfides, such as CuS , are decomposed only when the H_3PO_4 becomes concentrated, as it does in the latter part of the distillation. It is therefore directed in P. 107 and 112 to test also the second and third distillates for sulfide.

Procedure 106.—Detection of Cyanide.—Place what remains of the first distillate in a casserole; add 1–2 cc. 10% NaOH solution, about 0.5 cc. 10% FeSO_4 solution (or about 0.1 g. solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and 1 or 2 drops 10% FeCl_3 solution; and boil for one minute. To the hot mixture add HCl (1.12) a few drops at a time until on shaking the dark colored precipitate of ferrous and ferric hydroxides is dissolved. Cool the mixture. If a precipitate is not plainly visible, filter, and wash out the filter paper once with water. (Blue precipitate, presence of *cyanide*.)

Notes.—1. This test is based upon the formation of ferrocyanide by the action of cyanide on ferrous hydroxide and upon the reaction between this substance and the ferric salt whereby ferric ferrocyanide (Prussian blue) is formed, which is difficultly soluble in dilute hydrochloric acid.

2. A small precipitate is not readily detected in the hot reddish yellow solution, but is more easily seen in the cold light colored solution, especially after standing, or when collected on a filter. If the precipitate on the filter is not dark blue, it should be washed with a little hot, dilute hydrochloric acid. With these precautions, the test enables 0.2 mg. CN in the solution tested to be detected.

3. Cyanides may be present in the original substance in the form either of simple or of complex cyanides. The latter are characterized by complex anions (such as $\text{Ag}(\text{CN})_2^-$ and $\text{Fe}(\text{CN})_6^{3-}$). These differ very greatly in their stability towards decomposing agents, the difference depending on the extent to which they are disso-

ciated into the simple ions (Ag^+ and CN^- or Fe^{++} and CN^-). Ferrocyanides, ferricyanides, and cobalticyanides are so slightly dissociated in this way that scarcely any HCN is produced when dilute HCl , HNO_3 , or H_2SO_4 is added to their cold solutions; but almost all the other complex cyanides (such as $\text{KAg}(\text{CN})_2$ or $\text{K}_2\text{Ni}(\text{CN})_4$) are readily decomposed by these acids.

In the distillation with phosphoric acid (P. 101), not only the simple cyanides, but also nearly all the complex cyanides are decomposed during the first part of the distillation; but a few very stable substances (such as Prussian blue) are completely decomposed only in the second part of the distillation. A further test for cyanide with a portion of the second distillate is therefore necessary when such complex cyanides may be present.

4. The following procedure enables 2 mg. cyanide to be detected in the presence of ferro or ferricyanide: Place in a 20 cc. distilling flask provided with a thistle tube 0.5–1 gram of the original substance, 2 grams powdered CaCO_3 , and 10 cc. water. Add very gradually through the thistle tube 2 cc. HCl (1.12), enough to decompose some, but not all of the CaCO_3 . Allow the gas which is evolved to pass into a small test tube containing 3 cc. 10% NaOH and 3 cc. water. Finally heat the contents of the flask almost to boiling. Test the NaOH solution for cyanide by P. 106. This separation depends upon the fact that HCN is displaced by H_2CO_3 from simple cyanides and from the relatively unstable complex cyanides, such as $\text{Ag}(\text{CN})_2^-$ or $\text{Ni}(\text{CN})_4^{--}$, but not from ferro or ferricyanides.

5. Ferrocyanide and ferricyanide may be detected and distinguished from each other when only one of them is present, by adding a ferric salt to one portion of an aqueous or dilute acid solution, and by adding ferrous salt to another portion of the solution. A ferric salt gives a blue precipitate of ferric ferrocyanide with ferrocyanide, but no precipitate with a ferricyanide. A ferrous salt gives the same blue precipitate (of ferric ferrocyanide) with a ferricyanide; but it also gives with a ferrocyanide a precipitate (of ferrous ferrocyanide), which is white if no ferric salt is present, but which rapidly turns blue in contact with the air.

6. Ferrocyanide and ferricyanide may be detected in the presence of each other by proceeding as follows: Add to an aqueous or dilute solution of the substance AgNO_3 and then a moderate excess of NH_4OH . (White precipitate insoluble in NH_4OH , presence of ferrocyanide. Orange to red precipitate readily soluble in NH_4OH , presence of ferricyanide.) Filter out and wash the precipitate, and pour over it a little FeCl_3 solution. (Blue coloration, presence of ferrocyanide.) Acidify the ammoniacal filtrate with acetic acid, filter out and wash the precipitate, and pour through the filter containing it a little FeSO_4 solution (orange to red precipitate, which is turned blue by the FeSO_4 , presence of ferricyanide). This procedure enables 0.2 mg. $\text{Fe}(\text{CN})_6$ as either ferro or ferricyanide to be detected when present alone; but the test for ferricyanide is much less delicate in the presence of much ferrocyanide.

Analysis of the Second and Third Distillates.

Procedure 107.—*Detection of Constituents Precipitable by Silver Nitrate.*—To one-eighth of the second distillate add 1 cc. HNO_3 (1.20) and 1 cc. 4% AgNO_3 solution. (White precipitate, presence of *chloride, cyanide, or thiocyanate*; yellowish precipitate, presence of *bromide or iodide*; black precipitate, presence of *sulfide*; no precipitate, absence of all these in this distillate.)

If there is a precipitate, test separate eighths of the second distillate for sulfide by P. 105, for cyanide by P. 106 (see, however, Note 2), and for

thiocyanate by P. 108; and then test the remainder for free halogen and halides by P. 109 and 110, and for nitrate by P. 111.

If there is no precipitate, test the distillate for nitrate by P. 111.

Notes.—1. All the common silver salts, except the halides, cyanide, thiocyanate, and sulfide are either soluble in water (as are the nitrate, sulfate, chlorate, and fluoride) or dissolve readily in nitric acid owing to displacement of the weaker acid (as do the phosphate, carbonate, borate, and sulfite). It should be noted, however, that salts of weak acids are not necessarily readily soluble in a strong acid. Thus this is true of Ag_2S and AgCN , which are precipitated from this distillate, if H_2S and HCN are present in it. Silver sulfide does not dissolve in dilute nitric acid because its solubility in pure water is so extremely small that there is only a very minute concentration of S^{2-} ion in the saturated solution, and this can yield, in accordance with the mass action law, only a relatively small concentration of SH^- and unionized H_2S with the H^+ ion of the HNO_3 . Silver cyanide has for another reason a very slight concentration of its anion in its saturated solution, namely, owing to the fact that this salt exists in the solution mainly as Ag^+ and $\text{Ag}(\text{CN})_2^-$, and scarcely at all as Ag^+ and CN^- .

2. It is not necessary to test for sulfide and cyanide in this distillate when the original substance dissolved completely in the phosphoric acid during the first part of the distillation. When it does not so dissolve, H_2S and HCN (coming from complex cyanides) may be found wholly or in part in the second distillate.

Procedure 108.—Detection of Thiocyanate.—If AgNO_3 produced a precipitate (P. 107), dilute another eighth of the second distillate (P. 101) to 5–10 cc., add 2–3 drops of a 10% FeCl_3 solution and 2–3 drops of HCl (1.12). (Red color, presence of *thiocyanate*.)

Notes.—1. The red coloration arises from the formation by metathesis of $\text{Fe}(\text{SCN})_3$, a substance whose degree of ionization is relatively small. The HCl is added to reduce the hydrolysis of the FeCl_3 and diminish the color imparted by it to the solution.

2. A distinct reddish yellow coloration is produced by 0.1 mg. SCN . A deep red color is obtained when 1 mg. or more is present.

3. Since in the distillation with phosphoric acid, thiocyanates are destroyed by certain oxidizing agents, such as nitrates, which do not act on it at ordinary temperatures, it is sometimes advisable to apply this test also to a solution of the original substance.

Procedure 109.—Detection and Removal of Free Halogens.—If AgNO_3 gave a precipitate in P. 107, to two-thirds of the remainder of the second distillate in a separating funnel add 2–3 cc. chloroform and shake. (Purple color, presence of *iodine*; orange or yellow color, presence of *bromine*.)

If the chloroform is colorless, separate it from the aqueous layer. Add to the chloroform layer a few drops of 1% KI solution. (Purple color, presence of *chlorine*, or of *bromine* in small quantity.) If there is no color, treat the aqueous layer left in the separating funnel by P. 110.

If any free halogen is present, add to the mixture in the separating funnel 10 cc. chloroform, shake, and separate the two layers. Repeat the extraction with a fresh 10 cc. portion of chloroform. (Purple color of the chloroform layer and brown color of the aqueous layer, showing slow extraction of iodine, presence of *iodide*.) Test the aqueous layers for halides by P. 110.

If further tests for free bromine or chlorine are necessary, shake the chloroform extracts with 10 cc. water, adding enough H_2SO_4 solution to reduce the halogen, and treat the aqueous layer by P. 110.

Notes.—1. As to these tests see the notes to P. 103.

2. As there stated, the proportion of the iodine extracted from the aqueous layer by chloroform is much smaller when iodide is also present, so that some tri-iodide then remains in the aqueous solution after two extractions. Since this behavior itself shows the presence of iodide, it is not necessary to attempt to extract all the iodine before testing for halides by P. 110.

Procedure 110.—*Detection of Halides.*—Place the aqueous layer which is to be tested for halides (P. 109) in a separating funnel; add 3 cc. chloroform, 5 cc. 20% sodium acetate solution, 2 cc. 30% acetic acid, and 1 cc. 1% KMnO_4 solution (in excess of that required to oxidize any H_2SO_4 present), and shake. (Purple color, presence of *iodide*.) If there is a color, pour the mixture into a flask, add 10 cc. more CHCl_3 , and then add gradually 1% KMnO_4 solution, shaking after each addition, till the aqueous layer becomes pink. Pour the mixture through a moistened filter to remove the chloroform and precipitated MnO_2 , and shake the filtrate once or twice with a fresh 10 cc. portion of chloroform to extract all the iodine.

Place the aqueous solution and 3 cc. chloroform in a separating funnel, add 5 cc. H_2SO_4 (1.20), and 1 cc. 1% KMnO_4 solution, unless such an excess is already present, and shake. (Yellow or orange coloration of the chloroform, presence of *bromide*.)

Transfer the aqueous layer to a casserole, add 5–20 cc. 1% KMnO_4 solution, and boil the mixture 3–5 minutes, or until the volume has been reduced to 10 cc. Filter off the MnO_2 , and, if the solution is still pink, add H_2SO_4 solution drop by drop until it is colorless. Dilute the solution to 100 cc., filter if necessary, and add 2 cc. HNO_3 (1.20) and 1–2 cc. 4% AgNO_3 solution. (White precipitate, presence of *chloride*.)

Notes.—1. This separation is based upon the different rates at which KMnO_4 sets free by oxidation the three halogens from their salts in a solution of definite hydrogen-ion (H^+) concentration. A dilute solution of acetic acid containing considerable sodium acetate has such a hydrogen-ion concentration that an iodide is immediately oxidized by KMnO_4 with liberation of iodine, while bromide and chloride are not oxidized to an appreciable extent in the time required for the operations. When the H^+ -concentration is increased by the addition of the prescribed quantity of H_2SO_4 , the bromide is oxidized very rapidly while the rate of the corresponding reaction for the chloride is still so small at room temperature that scarcely any chlorine is set free. Even when the solution is boiled to expel the bromine, only a small fraction of the chloride present is oxidized to chlorine.

2. To secure satisfactory results, the directions as to the quantities of the acids added must be followed carefully. The proper quantity of H_2SO_4 is that required to react with all the sodium acetate, and in addition to give an excess equal to about 1 cc. H_2SO_4 (1.20) per 20 cc. of solution.

3. A very small precipitate of AgCl obtained at the end of the procedure does not necessarily indicate the presence of chloride in the substance, unless the reagents used have been proved to be entirely free from chloride. Even then a very slight precipitate

(corresponding to less than 0.1 mg. Cl) may result from a reaction between the permanganate and chloroform. For these reasons a blank test should be made in any doubtful case.

4. The yellow color of bromine in 3-5 cc. chloroform enables about 0.5 mg. Br to be detected in this procedure, which corresponds to 1-1.5 mg. Br in the whole of the second distillate. A much smaller quantity might be detected by separating the chloroform solution and adding KI solution to it; but when much chloride is present, this is an unreliable indication of bromide, since in that case an appreciable quantity of free chlorine may have been liberated by the permanganate. If it is desired to detect with certainty a smaller quantity of bromine, one may do so by treating the chloroform solution (obtained as described in the second paragraph of the above procedure), which contains the liberated bromine and perhaps a little chlorine, as follows: Shake it with 15 cc. water and 5 cc. H_2SO_4 (1.20), to which a few drops of saturated SO_2 solution are added; then add 1% KMnO_4 solution till the water layer becomes pink, and finally 1 cc. more. Shake well, separate the chloroform layer by means of a separating funnel, add to it a few drops KI solution, and shake again. A purple color shows the presence of bromide.

5. If HCN , H_2S , or HSCN are present in the distillate, they will be expelled or destroyed by the boiling with KMnO_4 before the final test for chloride with AgNO_3 is applied.

Procedure 111.—Detection of Nitrate.—To the remainder of the second distillate (after removing any iodide or thiocyanate present by shaking with solid Ag_2SO_4 and filtering) add 3 cc. H_2SO_4 (1.84) and 5 cc. saturated FeSO_4 solution. Place the mixture in the apparatus in P. 101, and distil until only about 5 cc. remain, collecting the distillate in a mixture of 20 cc. water and 2 cc. 10% NaOH . Make the distillate acid with H_2SO_4 , add 2-3 cc. chloroform and shake. If the chloroform is colorless, add a few drops of KI solution, and shake again. (Purple color, presence of nitrate.)

Notes.—1. In this procedure the nitrate is reduced by the FeSO_4 to nitric oxide (NO), which passes over as a gas into the receiver, where it is oxidized by the oxygen of the air to HNO_3 , which is then absorbed by the NaOH . When the solution is acidified and KI added, I_2 is liberated by the HNO_3 (see P. 103, N. 4). By this procedure 0.2 mg. NO_3 in the liquid submitted to distillation can be detected.

2. The reaction is highly characteristic for nitrates, since any nitrous acid present passed over completely into the first distillate, and since other oxidizing substances (for example, chlorine or bromine) which might liberate iodine from potassium iodide are reduced by the FeSO_4 to compounds which, even if they pass over into the distillate, have no action on KI. The only substances that may interfere are iodide and thiocyanate; and provision is therefore made for first removing these by adding solid Ag_2SO_4 , shaking, and filtering.

Procedure 112.—Detection of Sulfate.—To the third distillate obtained upon heating with copper (P. 101), add 1-2 cc. HCl (1.12), 5 cc. 2% BaCl_2 solution, and saturated Br_2 solution till the liquid becomes yellow. (White precipitate, presence of sulfate.)

Notes.—1. By the action of copper in the presence of concentrated H_3PO_4 on sulfates (even the very difficultly soluble BaSO_4) SO_2 is formed. This is oxidized by the Br_2 to H_2SO_4 , which then precipitates as BaSO_4 . In this way 1 mg. SO_4 may be

detected. Even when this small amount is present in the substance, only an inconsiderable proportion of it passes into the first and second distillates.

2. Much H_2PO_4 also passes over into the distillate; and the HCl is added to prevent its precipitation as BaHPO_4 . Too much HCl must not be added since BaSO_4 is appreciably soluble in it.

3. When a sulfide is present which has not already been decomposed, sulfur and H_2S may pass into the third distillate, after the acid has become concentrated. The H_2S may be tested for in a portion of the distillate by P. 105.

Supplementary Procedures.

Procedure 113.—Detection of Borate.—Place 1–2 grams¹ of the finely powdered substance in the distilling apparatus used in P. 101, and add 10 cc. of methyl alcohol (CH_3OH) and two or three glass beads. Pour in carefully 3 cc. H_2SO_4 (1.84), and distil off the alcohol, collecting it in a mixture of 5 cc. CH_3OH and 3 cc. HCl (1.20). Make the distillate up to 18 cc. with CH_3OH , cool, and add five drops of a saturated solution of turmeric in ethyl alcohol. (Red or orange color, presence of *borate*.) To estimate roughly the quantity present, compare the color with that given by adding the turmeric solution to known quantities of borate dissolved in a mixture of 3 cc. HCl (1.20) and 15 cc. CH_3OH .

Notes.—1. Methyl alcohol reacts with boric acid to form its methyl ester $\text{B}(\text{OCH}_3)_3$, which is a readily volatil liquid. The color given by turmeric to a solution of this ester in methyl alcohol and strong hydrochloric acid is so intense that the test is very delicate if the proportions given are reproduced. The presence of 1 mg. BO_2 in the substance distilled may readily be detected.

2. If the substance be distilled with H_2SO_4 and ethyl alcohol (instead of methyl alcohol), much less borate passes into the distillate, and the test is much less delicate.

Procedure 114.—Detection of Fluoride.—Mix 0.2 g. of the dry, finely powdered substance with twice its weight of powdered KHSO_4 and with 10–20 mg. dry, finely powdered or precipitated SiO_2 . Blow a thick-walled bulb $1\frac{1}{2}$ –2 cm. in diameter at the end of a glass tube of 5–8 mm. bore. Place the mixture in the bulb (not using more of it than will one-third fill the bulb). Heat the bulb carefully until the KHSO_4 is melted, taking care that the mixture does not froth up into the tube. Continue to heat the bulb and the lower part of the tube until there is a deposit of a solid substance or of condensed acid 3 or 4 cm. above the bulb. After it has cooled, cut off the tube close to the bulb. Dip the tube several times in water, dry it in a flame, and heat it strongly. (White deposit in the middle part of the tube and etched surface at the lower end, presence of *fluoride*.)

Notes.—1. This test depends on the following reactions:



¹ In this procedure and the subsequent ones, it is directed to take such an amount of substance as will enable 0.1–0.2% of the acidic constituent in question to be detected. The amount taken may of course be varied in accordance with the nature of the material and the object in view.

Some of the HF liberated by the molten KHSO_4 volatilizes and takes the silica required for the first reaction from the glass, thus producing the characteristic etched surface in the lower part of the tube. The SiF_4 gas and the water vapor liberated react in the cooler part of the tube according to the second equation, forming a white ring of solid silicic and fluosilicic acids in the tube. The reaction is reversed at higher temperatures, so that the deposit may be driven up the tube by heating. This white deposit is the most characteristic part of the test for fluoride, since in the subsequent washing H_2SiF_6 is removed and there remains H_2SiO_3 alone, which is converted into SiO_2 on heating. A deposit of SO_3 and H_2SO_4 may also form in the upper part of the tube, and might be mistaken for, or interfere with, the test for small amounts of fluoride, if the final washing with water is omitted. This procedure enables 0.5 mg. F to be easily detected.

2. The test fails with certain minerals which are not decomposed by fusion with KHSO_4 ; but such cases are provided for by the treatment described in P. 116.

3. Fluoride is often tested for by heating the solid substance in a platinum crucible with H_2SO_4 alone, and detecting any HF involved by its etching action on a watch glass coated with wax through which markings have been made. This test has the disadvantage that in the presence of silica or silicate, which is very often present in minerals, it is unreliable owing to the conversion of the HF to SiF_4 by the reaction given in note 1.

4. In distilling a fluoride with H_3PO_4 by P. 101, much of the HF reacts with the glass, but enough of it passes into the second distillate to enable 2–3 mg. F in the substance to be detected, if the whole distillate be tested with $\text{NaC}_2\text{H}_3\text{O}_2$ and CaCl_2 , as described in P. 116.

5. The precipitation of CaF_2 in an acetic acid solution from any source distinguishes fluoride from all the other acidic constituents except sulfate and oxalate, and is delicate enough to enable 0.2 mg. F in 10 cc. solution to be detected. The presence of fluoride in such a precipitate, even in a small one, can be confirmed by drying it, mixing it with a little KHSO_4 and SiO_2 , and heating as described in the procedure.

Procedure 115.—Detection of Phosphate.—To 0.1–0.2 g. of the finely powdered substance add about 5 cc. HNO_3 (1.20). If the substance does not dissolve, boil the mixture for 2 or 3 minutes, and filter. Add to the filtrate an equal volume of $(\text{NH}_4)_2\text{MoO}_4$ solution, and allow it to stand 5 to 10 minutes. (Yellow precipitate, presence of *phosphate*.)

Notes.—1. The yellow precipitate produced is a complex compound, ammonium phosphomolybdate, of a composition varying somewhat with the conditions, but approximating that represented by the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$.

2. In order that the test may be delicate, a large proportion of the $(\text{NH}_4)_2\text{MoO}_4$ must be present to reduce the solubility of the precipitate; and a short time must be allowed for the formation of the complex phosphomolybdate. This is promoted by gentle warming; but in a hot solution arsenate or silicate may give rise to a similar yellow precipitate, while in the cold the reaction is given only by phosphate. By this test 0.1 mg. PO_4 may be easily detected. The great delicacy of this test should be borne in mind in estimating the quantity of phosphate present.

3. Phosphate will have been detected in Part III (P. 63) of this system of analysis when elements of the iron, aluminum, or calcium groups are present.

Procedure 116.—Detection of the Acidic Constituents in Undecomposed Substances.—If the substance is not completely decomposed by acids (as shown in P. 101 and 115) heat 1 g. of the finely powdered substance with

HNO₃ (1.20), filter out and wash the residue, dry it, separate from the filter, and mix it with 5–10 g. dry Na₂CO₃ in a platinum crucible (or in a porcelain crucible, if reducible metals may be present in it). Cover the crucible and heat it over a powerful burner for 5–10 minutes. If a perfectly clear fusion does not result, add more Na₂CO₃, and heat again over a blast lamp. Cool, place the crucible in a casserole, boil it with water till the fused mass is disintegrated, and filter, rejecting the residue.

To a portion of the filtrate add HNO₃ (1.20) till it is distinctly acid, and test portions of it for *chloride* by adding AgNO₃, for *phosphate* by P. 115, and for *sulfate* by adding BaCl₂ solution.

Test another portion of the filtrate for *borate* by evaporating it to complete dryness, adding H₂SO₄ (1.84) drop by drop, and treating the mixture by P. 113.

Test a third portion of the filtrate for fluoride as follows: add 5 cc. 20% NaC₂H₃O₂ solution and 5 cc. 10% CaCl₂ solution, allow the mixture to stand 10–15 minutes. (White precipitate, presence of *fluoride*.) To confirm its presence, filter out, wash, and dry the precipitate, and test it by P. 114.

If silicate needs to be tested for, evaporate a portion of the solution, heat the residue at 100–125° till it is perfectly dry, add HCl (1.20) and boil gently. (White residue, presence of *silicate* or *silica*.) To confirm its presence, treat the residue by P. 5 (Part I).

Notes.—1. Fusion with Na₂CO₃ metathesizes nearly all insoluble compounds in the way described in the notes to P. 8 (Part I of this System of Analysis).

2. If basic elements that may be reduced to the metallic state (those of the silver, copper, and tin groups) may be present in the insoluble residue, it must be fused in a porcelain instead of a platinum crucible. It is, however, less desirable to use a porcelain crucible, since it is more difficult to attain the high temperature necessary, and since it is attacked by the flux and silicate is thereby introduced into the solution.

3. In minerals or metallurgical products undecomposed by acids, it is usually necessary to test only for silicate, chloride, sulfate, phosphate, borate, and fluoride, since other acidic constituents are scarcely ever present.

4. In a substance undecomposed by acids the presence of halides, sulfide, or sulfate can also be detected by proceeding as follows: Place about 0.10 g. of the solid substance in an iron tube about 15 cm. long and 1.5 cm. in outside diameter, or in a Jena glass tube, heat for 2–3 minutes to drive off water and to decompose unstable substances, cool and add 100 mg. freshly cut sodium. Heat the mixture strongly under a hood for 2–3 minutes, and allow to cool. Add 1 cc. methyl alcohol and after several minutes a little water, drop by drop. Then add 5 cc. water, shake and filter into a test tube. Acidify with acetic acid, and treat 1–2 cc. with AgNO₃ and HNO₃ (P. 107). If there is a precipitate, test one-third of the acetic acid solution for *sulfide* by adding 2 cc. 10% Cd(NO₃)₂ solution (P. 105), and test the remainder for *iodide*, *bromide*, and *chloride* by P. 110.

Compounds containing sulfur, even such stable substances as BaSO₄, MoS₃, CuS, are decomposed by this process with formation of sodium sulfide, and compounds containing chlorine, bromine, or iodine, even AgBr and AgI, are decomposed with formation of sodium halide. In the case of a substance of entirely unknown character,

only a small quantity (10–20 mg.) should be used at first, as the reaction with sodium might be a very violent one.

Procedure 117.—Detection of Hypochlorite.—To about 0.5 g. of the powdered substance mixed with 5 cc. water, or to 5 cc. of the alkalin solution, add acetic acid, a few drops at a time, until the solution is acid. Filter if there is much residue, add 2 cc. 20% lead acetate solution, heat the mixture to boiling, and let it stand for ten minutes. (Brown precipitate, presence of *hypochlorite*.)

Notes.—1. Hypochlorites are commonly met with either in alkalin solution or in the form of a powder (for example, in bleaching powder). Since they are prepared by the action of chlorine on alkali, chloride is ordinarily present in nearly equivalent amount. When the solid powder is treated with water, the hypochlorite passes into solution; and from it the unionized HClO is liberated upon the addition of the more largely ionized acetic acid. Chlorine is also formed until the equilibrium-conditions of the reaction $\text{HClO} + \text{Cl}^- + \text{H}^+ = \text{Cl}_2 + \text{H}_2\text{O}$ are satisfied. When in neutralizing with acetic acid litmus paper is used, the paper will soon be bleached if hypochlorite is present; but the color at the first instant or on the edges of the bleached portion can usually be observed.

2. This test depends upon the oxidation of the lead salt to lead dioxide PbO_2 , by the hypochlorite. The reaction takes place so slowly in the cold that not less than 10 mg. ClO in 5 cc. solution can be detected at room temperature, even if the mixture be allowed to stand a few minutes. But when the mixture is heated the limit of detectability is about 0.5 mg. in 5 cc. Since oxidation does not take place in the presence of a strong acid, such as HNO_3 , acetic acid is used in acidifying the solution.

3. Peroxides in alkalin solution react instantaneously with lead salts, forming PbO_2 ; but this reaction does not take place in the presence of acetic acid, even on boiling. Therefore in the above procedure a peroxide will not be mistaken for a hypochlorite. Peroxide and hypochlorite, moreover, cannot exist together, since they react very rapidly with formation of oxygen. If desired, peroxide may be tested for by treating the substance with a dilute acid and adding a few drops of a titanium sulfate solution (see P. 65b).

4. This test for hypochlorite may be made even more delicately in alkalin solution, provided peroxides are known to be absent. If the solution is only slightly alkalin, a small white precipitate of $\text{Pb}(\text{OH})_2$ or PbCO_3 is first formed; but this turns brown if hypochlorite is present when the mixture is heated and allowed to stand. The delicacy is of course diminished by the presence of large amounts of $\text{Pb}(\text{OH})_2$ or PbCO_3 ; but 1 mg. ClO can be detected in the presence of even 2 or 3 grams of these substances, provided an excess of the lead salt is still present in the solution, and the mixture is boiled vigorously, preferably in a casserole.

5. Hypobromite in alkalin solution or bromine in acetic acid solution also oxidizes lead salts to PbO_2 . Hypobromite is, however, so unstable that it will not be met with except in a solution freshly prepared from bromine and alkali. The results of previous tests will usually show whether HClO or Br_2 has given rise to the PbO_2 precipitate. In a doubtful case the halogens may be extracted by chloroform from an acid solution, and tested for by P. 109 and 110. On account of the equilibrium referred to in note 1 chlorine will be extracted in large proportion only if a strong acid or if much chloride is present.

Procedure 118.—Detection of Chlorate.—If chlorine has been found present in the first or second H_3PO_4 distillate, treat 0.5 g. of the sub-

stance in the cold with 50 cc. water and 10 cc. HNO_3 (1.20). (If hypochlorite is present as shown by P. 117, reduce it by adding Na_3AsO_3 solution in excess.) Add 4% AgNO_3 solution as long as a precipitate forms and then about 5 cc. more. Shake the mixture and filter off the precipitate. To the filtrate add 5 cc. saturated SO_2 solution, heat the mixture or allow it to stand five minutes. (White precipitate, presence of *chlorate* (or *bromate*).)

Notes.—1. In this procedure chlorate is reduced to chloride by the H_2SO_3 . The reaction is not instantaneous; but it is so rapid in the presence of a large excess of H_2SO_3 that at room temperature 1 mg. ClO_3 gives a distinct precipitate of AgCl within 5 minutes, even in a volume of 100 cc.

2. If iodate is present, it is precipitated upon the first addition of AgNO_3 , along with the silver halides; but if bromate is present, some of it remains in the solution and shows the same behavior as chlorate. If necessary to distinguish between them, the final precipitate with AgNO_3 may be treated as follows: Suspend it in 25 cc. water, pass in H_2S until the mixture is saturated with it, heat to boiling, filter off the precipitated Ag_2S , boil the filtrate till the H_2S is expelled, and test it for bromide and chloride by P. 110.

Procedure 119.—*Detection of Sulfite and Thiosulfate.*—If in P. 102 the first distillate was found to contain H_2SO_3 , add 0.5 gram of the finely powdered original substance to 5 cc. water and 1–5 cc. 10% Na_2CO_3 solution, shake the mixture, filter out any precipitate or residue, and add to the solution 3 cc. 10% $\text{Sr}(\text{NO}_3)_2$ solution, then at once add slowly 30% acetic acid, at the last a few drops at a time, until the precipitate of SrCO_3 dissolves on shaking, or until the solution reacts acid to litmus. Heat the mixture to boiling, add a drop or two of acetic acid if a flocculent precipitate forms, and let the mixture stand 15 minutes. (No precipitate, absence of *sulfite*.)

Filter out the $\text{Sr}(\text{NO}_3)_2$ precipitate, wash it once with a little cold water, pour a portion of 3–5 cc. HCl (1.06) two or three times through the filter, and add to the solution 5 cc. BaCl_2 solution. (If a precipitate of BaSO_4 forms, filter it out.) Then add to the solution saturated Br_2 solution till the liquid is slightly yellow. (Precipitate, presence of *sulfite*.)

To the filtrate from the $\text{Sr}(\text{NO}_3)_2$ precipitate, add 1–2 cc. HCl (1.20), heat the mixture to boiling, and let it stand overnight. (White turbidity or yellow precipitate, presence of *thiosulfate*.)

Notes.—1. Na_2CO_3 is added at the beginning of this procedure to separate from the acidic constituents in question any basic constituents present that may be precipitable by it. Its addition and the subsequent neutralization of it by acetic acid also serve to give a solution of small H^+ concentration, which is essential for a satisfactory separation of sulfite and thiosulfate. When the H^+ concentration is large, SrSO_3 dissolves and the thiosulfate decomposes with formation of sulfur; but in acetic acid solution the latter reaction is negligible even on heating in the presence of a considerable excess of the acid. SrSO_3 separates as a crystallin precipitate, slowly in the cold when present in small quantity, but much more rapidly when the mixture is heated. This procedure enables 1 mg. SO_3 in an initial volume of 10 cc. to be easily detected.

2. Upon the addition of a moderate excess of HCl over that required to react with all the sodium acetate present, the thiosulfate decomposes with the separation of sulfur. When 10 cc. of solution are treated by the above procedure, a precipitate of S forms within 30 minutes with 3 mg. S_2O_3 , and on standing over night with 1 mg. S_2O_3 .

Confirmatory Experiments.

P. 101-112. *Test Analysis*.—A mixture of 2 mg. of each of the constituents CN, Cl, Br, I, NO_3 , SO_4 , SO_3 , CO_3 , as the sodium or potassium salt, was dissolved in 2 cc. water and tested according to P. 101-112: distinct and satisfactory tests were obtained for each constituent.

P. 101. *Distillation with Phosphoric Acid*.—The experiments tabulated below were carried out to determine the behavior of the various acidic constituents in the phosphoric acid distillation. The division into first and second distillates corresponds to that given in P. 101. The substances taken are given in the first column, the substances tested for in the distillates are given in the second column, and the results of the tests are given in the third and fourth columns. The numbers in the last two columns show the amount of substance estimated to be present in the distillates. The letter S denotes that the test was satisfactory, and that the amount of substance found seemed to correspond to that taken.

Substance taken.	Constituent tested for	First distillate.	Second distillate.
2 mg. Cl as NaCl.....	{ Chloride	o	S
	{ Chlorine	o	o
1500 mg. Cl as NaCl.....	Chlorine	o.1	o
15 mg. Cl as AgCl.....	Chloride	o	3-5
1 mg. Cl_2 as bleaching powder.....	Chlorine	S	o
1 mg. Br as KBr.....	Bromide	..	S
1500 mg. Br as KBr.....	{ Bromide	small	S
	{ Bromine	..	o.5
100 mg. Br as AgBr.....	{ Bromide	o	o
	{ Bromine	o	o
2 mg. Br_2	Bromine	S	o
1 mg. I as KI.....	Iodide	..	S
100 mg. I as AgI.....	{ Iodide	o	o
	{ Iodine	o	o
100 mg. F as NH_4F	Fluoride	2-4	20-30
3 mg. F as KF.....	Fluoride	o	small
2 mg. F as KF.....	Fluoride	o	slight
100 mg. F as CaF_2	Fluoride	o	4-5
1 mg. SCN as KSCN.....	Thiocyanate	slight	S
2 mg. SCN as KSCN.....	Thiocyanate	small	S
1000 mg. SCN as KSCN.....	{ Thiocyanate	large	large
	{ Sulfide	small	small ¹
1 mg. CN as KCN.....	Cyanide	S	o
2 mg. $Fe(CN)_6$ as $K_4Fe(CN)_6$	Cyanide	S	o
5 mg. $Fe(CN)_6$ as $K_4Fe(CN)_6$	Cyanide	S	o
500 mg. $Fe(CN)_6$ as $K_4Fe(CN)_6$	{ Cyanide	large	large
	{ Ferrocyanide	o	o
	{ Ferricyanide	o	o
2 mg. $Fe(CN)_6$ as $K_3Fe(CN)_6$	Cyanide	slight	o

¹ Some free sulfur was also present.

Substance taken.	Constituent tested for	First distillate.	Second distillate.
5 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_3\text{Fe}(\text{CN})_6$	Cyanide	small	o
600 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_3\text{Fe}(\text{CN})_6$	Cyanide	large	large
	Ferrocyanide	o	o
	Ferricyanide	o	o
700 mg. Prussian blue.....	Cyanide	large	large
100 mg. S as CuS	Sulfide	o	trace ¹
100 mg. S as FeS	Sulfide	large	small
900 mg. galena.....	Sulfide	large	large
700 mg. pyrite.....	Sulfide	o	large ¹
710 mg. MoS_2	Sulfide	o	o
1 mg. NO_2 as NaNO_2	Nitrite	S	..
20 mg. NO_2 as NaNO_2	Nitrite	S	..
1 mg. SO_2 as Na_2SO_3	Sulfite	doubtful	o
2 mg. SO_2 as Na_2SO_3	Sulfite	S	o
20 mg. SO_2 as Na_2SO_3	Sulfite	S	o
400 mg. C_2O_4 as $(\text{NH}_4)_2\text{C}_2\text{O}_4$	Carbonate	o	large
5 mg. ClO_2 as KClO_2	Chloride	o	slight
	Chlorine	slight	o
1500 mg. ClO_2 as KClO_2	Chloride	o	large
	Chlorine	slight	large
45 mg. BrO_2 as KBrO_2	Bromide	large	large
	Bromine	large	large
50 mg. S_2O_3 as $\text{Na}_2\text{S}_2\text{O}_3$	Sulfide	large	small
	Sulfur	small	small
2 mg. S_2O_3 as $\text{Na}_2\text{S}_2\text{O}_3$	Sulfide	S	..

P. 101, N. 4. *Detection of Carbonate*.—Several experiments were made in which the first distillate was collected in a weakly ammoniacal solution. It was found that the addition of $\text{Ba}(\text{OH})_2$ often failed to precipitate small amounts of carbonate, especially when the NH_4OH had been first neutralized with acetic acid.

P. 101, N. 5 and 9. *Action of Phosphoric Acid and Copper on Sulfates*.—100 mg. SO_4 as Na_2SO_4 were placed in a distilling flask together with 10 cc. of H_3PO_4 and 3–4 grams of fresh Cu turnings, and the mixture was boiled down to the point where faint fumes were first seen: the distillate was found to contain neither H_2SO_4 nor H_2SO_3 . The distillation was then continued 3 to 5 minutes longer and the vapors collected in water: the distillate now smelled strongly of SO_2 and on adding HCl , Br_2 , and BaCl_2 (P. 112) a large precipitate was obtained. This experiment was repeated with 1 mg. SO_4 , except that the distillate was collected in a dilute NaOH solution: a precipitate of BaSO_4 was obtained in P. 112, which was estimated to be equivalent to the SO_4 taken. The experiment was repeated with no sulfate: a satisfactory blank test resulted. The experiment was repeated with 125 mg. and with 2 mg. SO_4 as precipitated BaSO_4 , the vapors being collected in water; the BaSO_4 precipitates in P. 112 were estimated to contain 20 mg. and 2 mg. SO_4 , respectively.

P. 101, N. 8. *Absorption of Carbon Dioxide from the Air*.—10 cc. H_3PO_4 were added to 25 cc. water, the mixture was placed in the distilling flask and boiled 2–3 minutes, the distillate being collected in nearly saturated solution of $\text{Ba}(\text{OH})_2$ contained in a 100 cc. flask fitted with a two hole stopper: a small but distinct precipitate was obtained, becoming larger on cooling. The outlet hole of the receiving flask was fitted with a small soda-lime tube and the distillation repeated: a small precipitate was again

¹ Some free sulfur was also present.

obtained. 10 cc. H_3PO_4 were mixed with 20 cc. water, the mixture was brought to boiling and was then added through the upright safety tube to the distilling apparatus to which the receiving $\text{Ba}(\text{OH})_2$ flask had previously been attached: on distilling a few minutes only a very slight turbidity appeared in the $\text{Ba}(\text{OH})_2$ solution.

P. 101, N. 7. *Separation of Carbonate and Sulfite*.—Three 15 cc. samples, containing 3 mg. SO_3 and 0, 1, and 2 mg. CO_3 , respectively, were treated with 3 cc. of a 'saturated' $\text{Ba}(\text{OH})_2$ solution acidified with $\text{HC}_2\text{H}_3\text{O}_2$, with 1 cc. HCl (1.12), and with bromine water till distinctly yellow. The different samples were then distilled into a $\text{Ba}(\text{OH})_2$ solution. The first gave a slight turbidity, the second a pronounced turbidity, and the third a distinct precipitate of BaCO_3 .

Several attempts were made to effect the separation of sulfite from carbonate by filtering out BaSO_3 from an acetic acid solution of the carbonate. It was not found possible to prevent the finely divided sulfite from passing through the filter.

P. 103, N. 2. *Distribution Ratios*.—Approximate values of the distribution ratio of iodine and bromine at 25° between certain organic solvents and water are given in the following table:

Solvent.....	CCl_4 .	CHBr_3 .	CS_2 .
Distribution ratio for iodine.....	85	450	600
Distribution ratio for bromine.....	30	66	80

Jakowkin's data¹ show that the change with the concentration of the halogen is small. From the solubility determinations of Bruner,² it seems probable that the distribution ratios for CHCl_3 lie between those for CCl_4 and CHBr_3 .³

According to Jakowkin,⁴ the distribution ratio of the molecular species Cl_2 between CCl_4 and water is 20 at 25° , but that of the total dissolved chlorine is much less at small concentrations; thus it becomes less than unity when the chlorine concentration in water is as small as 2.6 millimols per liter.

The Hydrolysis of Chlorine.—See Jakowkin, *Z. physik. Chem.*, 29, 613 (1899).

The Hydrolysis of Iodine and Bromine.—See Bray, *THIS JOURNAL*, 32, 932 (1910); 33, 1485 (1911).

Potassium Tri-iodide.—See Jakowkin *Z. physik. Chem.*, 20, 19 (1896); and Bray and Mackay, *THIS JOURNAL*, 32, 914 (1910).

P. 103, N. 3. *Delicacy of the Tests for Halogens*. *Iodine*.—0.5 mg. I_2 was dissolved in 8 cc. water and 2 cc. 85% H_3PO_4 and shaken with 3 cc. chloroform: the chloroform had a faint but distinct pink color.

Bromine.—0.7 and 0.5 mg. Br_2 were dissolved in 8 cc. water and 2 cc. H_3PO_4 and shaken with 3 cc. chloroform: the chloroform layer had a faint but distinct yellow color in each case. The experiment was repeated with 0.3 mg. Br_2 : the test was unsatisfactory, since the faint yellow color of the chloroform could be observed only by comparison with pure chloroform. The limit for this test is therefore about 0.5 mg. Br_2 in 3 cc. CHCl_3 .⁶

A third of the aqueous phase in the preceding experiment with 0.7 mg. Br_2 was carefully poured into a test tube containing 1 cc. 1% KI solution, and 1 cc. chloroform was added and the mixture shaken. The aqueous solution was practically colorless, but the chloroform showed a very faint pink color. The experiment was repeated

¹ *Z. physik. Chem.*, 18, 588–90 (1895).

² *Ibid.*, 26, 147 (1898).

³ Cf. Seidell's "Solubilities."

⁴ *Z. physik. Chem.*, 29, 634–6 (1899).

⁵ In the first form of the Procedure, phosphoric acid was added in place of acetic acid, but this could hardly influence the delicacy of the tests.

⁶ Cf. C. E. P., 110.

except that the water-chloroform mixture (containing bromine) was shaken before pouring one-third of it into the KI solution: the aqueous layer was yellow and the chloroform layer pink. This last experiment was repeated with the above mixture containing 0.3 mg. Br_2 : the aqueous layer was faintly yellow and the chloroform distinctly pink, thus showing that a smaller quantity of bromine could have been detected in this procedure.

Bromine in the First Distillate.—2 mg. Br_2 were added to 5 cc. $\text{Ba}(\text{OH})_2$ solution, the mixture was heated, cooled, and acidified with acetic acid, an excess of 1 cc. being added. The mixture having a volume of 10 cc. was shaken with 2–3 cc. chloroform: a distinct yellow color resulted, which corresponded to about 1 mg. Br_2 . The experiment was repeated with 1 mg. Br_2 : a faint yellow color resulted, which corresponded to about 0.5 mg. Br_2 . The yellow color disappeared on standing, and special experiments showed that the chief loss was due to volatilization. The experiment was repeated with 10 mg. Br_2 , the Br_2 was extracted 3 times within 3 min., and KI solution and chloroform added to the aqueous layer: a slight pink coloration resulted, which corresponded to about 0.2 mg. Br_2 . This showed that the reaction between bromate and bromide in acetic acid solution was so rapid that the apparent loss of bromine in the first experiments could not be attributed to the presence of bromate.

The first experiment in the preceding paragraph was repeated with 0.3 mg. Br_2 and with 0.2 mg. Br_2 : the chloroform layer was colorless. The mixture was shaken and one-third of it added to a KI solution: the chloroform layer showed a faint but distinct pink color in the first case, but not in the second.

Chlorine.—An amount of bleaching powder containing 1 mg. of available chlorine was treated by P. 101; one-fifth of the distillate was acidified with acetic acid and a few drops of KI solution were added: a distinct liberation of iodine was observed.

A solution containing 20 mg. Cl_2 dissolved in 8 cc. water and 2 cc. 10% NaOH solution was acidified with acetic acid and 5 cc. HNO_3 (1.20) were added. The mixture was shaken with 2 cc. CHCl_3 and then with 3 cc. The amount of chlorine extracted was estimated to be about 12 mg. by adding a little KI solution to the chloroform. A third treatment with CHCl_3 extracted 3 mg. Cl_2 , and the amount remaining in the solution (5 mg.) was estimated by adding chloroform and a little KI solution to the aqueous phase. The experiment was repeated three times, except that 2 cc. 30% acetic acid were added instead of 5 cc. HNO_3 (1.20): the amounts of chlorine extracted in the first two treatments with CHCl_3 were estimated to be 4, 6, and 6 mg., respectively, in the three experiments.

P. 103, N. 4. *Delicacy of the Iodide Test for Nitrous Acid.*—0.1 mg. NO_2 as NaNO_2 was added to 10 cc. water and 1 cc. 30% acetic acid; KI solution and chloroform were added and the mixture shaken; the mixture was allowed to stand 10 min. and again shaken. A distinct pink color was produced at once, and the depth of color increased on standing.

Distribution of Nitrous Acid between Water and Chloroform.—2.0 mg. NO_2 as NaNO_2 were added to 10 cc. water and 1 cc. acetic acid, and the mixture was extracted twice with chloroform; KI was then added to the chloroform layer: an amount of iodine was liberated which corresponded to less than 0.1 mg. NO_2 . The experiment was repeated with 15 mg. NO_2 : a very distinct test for iodine was obtained when KI was added to the chloroform layer, and the amount of iodine increased on standing.

P. 103, N. 5. *Action of Bromine and Iodine on Nitrous Acid.*—3.5 mg. Br_2 in 1 cc. water were added to 2 cc. of a 1% solution of NO_2 as NaNO_2 : the color of the bromine disappeared immediately. The same result was obtained in the presence of acetic acid.

To a solution of 1 mg. NO_2 as NaNO_2 in water containing 1 cc. acetic acid, an ex-

cess of I_2 was added. After 10 minutes the solution was extracted three times with fresh portions of $CHCl_3$, and the aqueous layer was then shaken with fresh $CHCl_3$ and KI solution: there resulted a slight pink color, corresponding to 0.2 mg. I_2 .

10 mg. NO_2 as $NaNO_2$ and 10 mg. I_2 (about one-fifth of the amount necessary to oxidize the nitrite to nitrate) in 10 cc. H_2O were distilled with dilute H_3PO_4 according to P. 101. The first distillate was collected in barium hydroxide solution and acidified with acetic acid: it gave no test for nitrous acid with urea by P. 104, and a strong test for I_2 on extracting with $CHCl_3$.

P. 103, N. 6. See above, N. 2 and 3.

P. 104, N. 2. *Delicacy of the Urea Test for Nitrite.*—0.1 mg. NO_2 as $NaNO_2$ in 1 cc. H_2O was added to a 20% solution of urea in HCl (1.12): a large number of very minute bubbles formed slowly and rose to the top of the inverted tube. The experiment was repeated with 1.0 mg.: the bubbles formed quickly and united to a large bubble at the top of the tube. The experiment was repeated with 1 cc. water which had been shaken with air: a few minute bubbles appeared at once, but not nearly so many as in the experiment with 0.1 mg. NO_2 . The same experiments were tried with a 20% solution of urea in H_2SO_4 (1.20): the results were the same.

P. 104, N. 3. *Behavior of Halogens in the Urea Test for Nitrite.*—10 mg. Br_2 were dissolved in 1 cc. $Ba(OH)_2$ solution and added to a solution of urea in HCl: a few minute bubbles (of air) appeared, which corresponded in amount to the test with 1 cc. water (preceding paragraph). The experiment was repeated, except that the solution of Br_2 in $Ba(OH)_2$ was first acidified with HCl: the result was the same. The last experiment was repeated with a solution of chlorine, using a 20% solution of urea in H_2SO_4 : there was no evolution of gas.

P. 105, N. 2. *Decomposition of Difficultly Soluble Sulfides by Phosphoric Acid.*—See C. E. P., 101.

P. 106, N. 2. *Delicacy of the Test for Cyanide.*—Several separate solutions containing 0.1 and 0.2 mg. CN as KCN in 10 cc. were tested by P. 106. A good test was invariably found with 0.2 mg. and sometimes with 0.1 mg. The experiment with 0.2 mg. CN was repeated except that the $FeCl_3$ was added after boiling: a good test was obtained. The last experiment was twice repeated except that 4.0 cc. 10% NaOH solution were added instead of 1.0 cc.: the test was very satisfactory but seemed slightly less distinct than before.

P. 106, N. 3. *Relative Solubilities of Complex Cyanides.*—See Abegg and Bodländer, *Z. anorg. Chem.*, 20, 453 (1899). Böttger, *Qual. Analyse*, 287, 289, 291, 191, 391, 396, and 432-5 (1908).

P. 106, N. 4. *Delicacy of the Test for Cyanide in the Presence of Ferro and Ferricyanide.*—2 mg. CN as KCN were tested by the procedure described in Note 4: a distinct test for cyanide was obtained in the distillate. The experiment was repeated first with 30 mg. $Fe(CN)_6$ as $K_3Fe(CN)_6$ and then with 30 mg. $Fe(CN)_6$ as $K_4Fe(CN)_6$: no CN was found in the distillate in either experiment. The experiment was repeated with a mixture of 2 mg. CN as KCN and 40 mg. $Fe(CN)_6$ as $K_3Fe(CN)_6$: a distinct test for CN was obtained in the distillate.

P. 106, N. 5. *The Blue Iron-cyanide Compounds.*—Hofmann, Heine and Höchtlen, *Liebig's Ann.*, 337, 1 (1904).

P. 106, N. 6. *Separation of Ferro and Ferricyanides.*¹—To 0.2 mg. $Fe(CN)_6$ as $K_4Fe(CN)_6$ in 10 cc. water were added a little acetic acid, 1 cc. 4% $AgNO_3$ solution, and finally excess of NH_4OH : a small white precipitate formed in the acid solution and did not dissolve on the addition of NH_4OH . This was collected in a filter, washed with water and moistened with a dilute solution of $FeCl_3$: the precipitate turned blue

¹ See also Böttger, *Qual. Analyse*, 392, 292 (1908).

at once. The experiment was repeated with 0.2 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_3\text{Fe}(\text{CN})_6$: A small brown precipitate formed in the acid solution but dissolved in NH_4OH . On acidifying with acetic acid, filtering, washing with water, and adding FeSO_4 solution the precipitate turned blue. The last experiment was repeated several times with 50 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_4\text{Fe}(\text{CN})_6$ and 1 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_3\text{Fe}(\text{CN})_6$: the test for ferricyanide failed. 50 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_4\text{Fe}(\text{CN})_6$ and 1 mg. $\text{Fe}(\text{CN})_6$ as $\text{K}_3\text{Fe}(\text{CN})_6$ were dissolved in 10 cc. water, 2 cc. 1% KI solution, and 2 cc. chloroform were added, and HCl (1.20) was added drop by drop: on shaking, the chloroform layer became purple.

P. 110. *Separation and Detection of the Halogens. Test Analyses.*—Known amounts of KI, KBr, and KCl were dissolved in about 15 cc. water, and the mixtures were analyzed by P. 110. The following table shows the milligrams of I, Br, and Cl taken in each experiment, and the results obtained. The letter S signifies that the test or the blank was satisfactory. This was found to be true in every case.

Expt.	1.	2.	3.	4.	5.	6.	7.	8.	9.
I . . .	1 S	0.5 S	100 S	100 S	100 S	100 S	0 S	0 S	0 S
Br . . .	0—	0—	0 S	1 S	0 S	1 S	0 S	100 S	100 S
Cl . . .	0—	0—	0 S	0 S	500 S	500 S	1 S	0 S	1 S

Liberation of Bromine in the Iodide Test.—To solutions containing 100 mg. Br as KBr dissolved in 15 cc. water were added 5 cc. CS_2 , known amounts of a 10% sodium acetate solution, 1 cc. 30% acetic acid, and 20 cc. 0.1 N KMnO_4 solution; after 1 hour the mixtures were shaken, the CS_2 was drawn off, and the amount of Br_2 liberated was estimated from the color of the CS_2 : with 1 cc. 10% acetate solution about 5 mg. Br_2 were liberated; with 2 cc. about 1 mg.; and with 5 cc. not enough Br_2 to give a color to the CS_2 . In the last experiment, the proportion of acetate to acetic acid was the same as in the Procedure, but the KMnO_4 added and the time allowed was much greater. The result obtained therefore shows that there is no danger of liberating Br_2 under the conditions of the Procedure.

Action of Permanganate on Iodide to Form Iodate.—50 mg. I as KI in a volume of 15 cc. were treated with 5 cc. 10% $\text{NaC}_2\text{H}_3\text{O}_2$, 1 cc. 30% $\text{HC}_2\text{H}_3\text{O}_2$, and 15 cc. 0.1 N KMnO_4 solution (in the absence of CS_2). After standing 10 minutes the mixture was shaken several times with CS_2 until the last CS_2 portion was colorless. The water layer was treated with H_2SO_4 until colorless, allowed to stand 5 minutes, and then tested with CS_2 and KMnO_4 as described in the procedure: a very satisfactory test for iodide was obtained. This shows that iodate had been formed by the action of KMnO_4 on iodine (or iodide), and that the iodate was reduced by the treatment with H_2SO_4 . The experiment was repeated with 1 mg. I as KI: no iodine was extracted by the first treatment with CS_2 , thus showing that the initial presence of CS_2 and shaking are essential if a small amount of iodide is to be detected when excess of KMnO_4 is added. The experiment with 50 mg. I as KI was repeated except that CS_2 was initially present and that the iodine was extracted at once instead of after 10 minutes: some iodate was formed, but much less than in the above experiment.

Effect of Iodate on the Bromide Test.—A solution containing 100 mg. Br as KBr and 500 mg. KIO_3 in 20 cc. was treated with 5 cc. 10% $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. 30% $\text{HC}_2\text{H}_3\text{O}_2$, and allowed to stand 10 minutes. The mixture was shaken with 5 cc. CHCl_3 , and the CHCl_3 layer was drawn off and tested with a few drops of KI: there was no color, thus showing that no bromine would be liberated in the iodide test owing to the presence of iodate. 5 cc. chloroform and 5 cc. H_2SO_4 (1.20) were then added to the aqueous layer: bromine was liberated in large amount. The experiment was then repeated with 1 mg. Br as KBr and 500 mg. KIO_3 . After adding the H_2SO_4 the CHCl_3 layer showed the bromine color, and iodine was liberated on adding a few drops KI to the

CHCl_3 layer. This shows that the presence of iodate does not interfere with the test for bromine.

Liberation of Chlorine in the Bromide Test.—500 mg. Cl as NaCl in a volume of 15 cc. were treated with 1 cc. H_2SO_4 (1.20) and 5 cc. 0.2 N KMnO_4 , allowed to stand 30 minutes, and extracted with 5 cc. CHCl_3 ; the CHCl_3 was colorless, and on adding a few drops of KI the small amount of iodine liberated was estimated to correspond to about 0.3 mg. Cl_2 . A solution containing 500 mg. Cl as NaCl and 100 mg. KIO_3 in 15 cc. was treated with 2 cc. H_2SO_4 (1.20) and 15 cc. 0.1 N KMnO_4 solution, and 5 cc. CHCl_3 were added: the CHCl_3 layer remained colorless. After 5 minutes the mixture was shaken, the CHCl_3 drawn off and treated with a few drops of KI solution: the purple color showed the presence of about 0.2 mg. Cl_2 . 5 cc. more CHCl_3 were then added and tested in the same way with KI after 25 minutes: the amount of iodine liberated showed the presence of about 1 mg. Cl_2 . These experiments show that the liberation of chlorine in the bromide test is very slow, even in the presence of iodate and of large amounts of chloride. There is, therefore, no danger of oxidizing a small amount of chloride completely to chlorine.

Complete Removal of Bromide by Boiling.—A solution of 150 mg. Br as KBr in 20 cc. was treated with 2 cc. of H_2SO_4 (1.20) and 18 cc. of 0.2 N KMnO_4 , and boiled for about 2 minutes until the odor of bromine could no longer be detected. The solution was filtered and treated with 2 cc. of H_2SO_4 and 5 cc. of KMnO_4 , allowed to stand 5 minutes, and extracted with CHCl_3 : no bromine was found.

Non-Removal of Chloride by Boiling with Permanganate in the Presence of Sulfuric Acid.—1 mg. Cl as chloride in 20 cc. was treated with 3 cc. H_2SO_4 (1.20) and 15 cc. of 0.2 N KMnO_4 , boiled for 3 minutes, and extracted with CHCl_3 ; the water layer was diluted, treated with H_2SO_4 to decolorize the excess of KMnO_4 , and to it AgNO_3 and HNO_3 were added: a distinct precipitate was formed, while a blank test carried out in a similar manner gave only a slight turbidity at this point.

Non-Effect of Thiocyanate on the Test for Chloride.—A solution of 20 mg. SCN as KSCN in 20 cc. was treated with 3 cc. of H_2SO_4 (1.20) and with 12 cc. of 0.2 N KMnO_4 : this was decolorized as fast as it was added, with separation of MnO_2 ; and the clear colorless filtrate gave no color on adding FeCl_3 , nor any precipitate on treating with HNO_3 and AgNO_3 .

Delicacy of the Color Test for Free Bromine in Chloroform and Other Solvents.—1, 0.5, 0.3, and 0.0 mg. Br as KBr in 20 cc. water were each treated with 2 cc. of H_2SO_4 (1.20) and 1 cc. of 0.2 N KMnO_4 ; after standing 10 minutes each solution was extracted with 5 cc. CHCl_3 , and the chloroform layer washed once with water: the 1 mg. sample gave a pronounced color to the CHCl_3 , the 0.5 mg. one gave a distinct but faint color. Similar experiments with CS_2 and CCl_4 gave similar results; but the tests with these solvents seemed to be a little less delicate than with CHCl_3 .

P. 111, N. 1. *Delicacy of Nitrate Test.*—0.2 mg. NO_3 as NaNO_3 in 10 cc. water were treated by P. 111: a distinct liberation of iodine in the distillate resulted on adding H_2SO_4 and KI. 2 mg. NO_3 were treated by P. 101, and one-third of the distillate from this procedure was treated by P. 111: a good test for nitrate was obtained.

P. 111, N. 2. *Interference of Iodide with the Nitrate Test and Its Removal.*—50 mg. I as KI were put through P. 111. On making the distillate acid a large amount of iodine was liberated.

50 mg. I as KI and 0.3 mg. NO_3 as NaNO_3 in 10 cc. water were treated with 15 cc. of a nearly saturated $\text{AgC}_2\text{H}_3\text{O}_2$ solution, boiled 1 minute, allowed to stand a short time, and filtered; and the filtrate was treated by P. 111: on making the distillate acid with H_2SO_4 no iodine was liberated and on adding a few drops of KI solution a distinct yellow color was given to the mixture. This experiment was repeated with 50 mg.

I and no NO_2 : a little color due to liberated iodine was observed in the final test, but distinctly less than in the preceding experiment with 0.3 mg. NO_2 . This small test was later shown to be due to a trace of nitrate existing as impurity in the $\text{AgC}_2\text{H}_3\text{O}_2$ used.

Non-Interference of Cyanide in the Nitrate Test.—A solution of 100 mg. CN as KCN and 1 mg. NO_2 as NaNO_2 in 10 cc. water was treated by P. 111: a small but distinct color resulted in the distillate on adding acid and KI. The experiment was repeated with 100 mg. CN as KCN and no NO_2 in 10 cc. water: the distillate treated with acid and KI gave no color.

Interference of Thiocyanate in the Nitrate Test.—0.5 mg. NO_2 as NaNO_2 and 100 mg. SCN as KSCN in 10 cc. water were treated by P. 111: the distillate smelled strongly of H_2S and gave no liberation of iodine when treated with acid and KI.

P. 112, N. 1. *Delicacy of Test for Sulfate.*—See C. E., P. 101, N. 5 and 9.

P. 113, N. 2. *Delicacy of the Borate Test.*—2 mg. BO_2 as $\text{Na}_2\text{B}_4\text{O}_7$ were treated by P. 113: a distinct color resulted. On setting fire to the orange tinted solution to which the turmeric had been added, no green color was noticeable in the flame. The experiment was repeated with 5 mg. BO_2 : a good test with turmeric was obtained; and a flash of green could be seen just at the moment of setting fire to the solution.

P. 113, N. 2. *Use of Ethyl Alcohol in the Borate Test.*—5 mg. BO_2 as $\text{Na}_2\text{B}_4\text{O}_7$ were treated by P. 113, except that $\text{C}_2\text{H}_5\text{OH}$ was substituted for the CH_3OH : the color obtained with turmeric was so slight as to be doubtful.

P. 114. *The Test for Fluoride.*—This method was described by Berzelius. The directions in P. 114 are similar to those given by Brush-Penfield, *Determinative Mineralogy and Blowpipe Analysis*.

A known small amount of F as powdered fluorite, CaF_2 , mixed with a few milligrams powdered SiO_2 and about 50 mg. powdered KHSO_4 , was heated in a small bulb blown on a tube of 5 mm. bore, and was treated as described in the Procedure: there was a ring of SiO_2 in the tube about 4 cm. from the bulb, and the etching in the lower part of the tube was very distinct even in the experiment with 0.5 mg. F. The experiment with 0.5 mg. F as CaF_2 was repeated with no silica but in the presence of 500 mg. KHSO_4 and with a large bulb: the ring test was small but distinct, but the etching test was unsatisfactory. Several experiments were tried in the absence of CaF_2 : satisfactory blanks were always obtained.

The experiment was repeated with 20 mg. CaF_2 , 20 mg. SiO_2 and about 100 mg. KHSO_4 . The tube was closed by a small rubber stopper through which a small capillary tube moistened on the inside passed to about 4 cm. from the bulb: there was a heavy ring of deposited solid in the entrance to the capillary and on the wall of the outside tube near the end of the capillary tube. This indicates that there is no tendency for the SiF_4 to escape from the tube. The experiment was repeated with 0.5 mg. F as CaF_2 : there was a distinct ring test on the wall of the large tube, but none in the capillary tube. There is therefore no advantage in inserting the moist capillary.

P. 114. *Modification of the Fluoride Test.*—4, 2 and 1 mg. F as solid CaF_2 were mixed with 50–100 mg. ignited precipitated SiO_2 in a dry weighing tube, and 8–10 drops H_2SO_4 (1.84) were added; a wet glass rod with a drop of water hanging from it was suspended from a stopper in the tube, and the mixture was warmed gently: upon heating there was in each case a distinct effervescence, and in the 4 mg. and 2 mg. experiments the wet walls of the rod, but not the drop of water, became distinctly opaque; in the 1 mg. experiment, the opaqueness produced was so slight as to be doubtful, thus showing that this form of the test is less delicate than that described in the Procedure.

P. 116, N. 4. *Reaction between Sodium and Certain Insoluble Substances.*—See Mulliken, *Identification of Organic Compounds*, Vol. 1.

2 mg. AgI were fused with sodium as described in P. 116, N. 4, and the solution tested by P. 110: a distinct test for iodide was obtained. 16 mg. BaSO₄ were fused with sodium, and the acetic acid solution was treated by P. 105: a large yellow precipitate of CdS formed. The last experiment was repeated with 4.4 mg. S as MoS₃ (molybdenite): a CdS precipitate was obtained, whose size indicated the complete decomposition of the MoS₃.

P. 117, N. 2 and 4. *Delicacy of the Test for Hypochlorite.*—In each experiment a known amount of an alkaline NaClO solution (made by treating a known weight of bleaching powder with a small excess of Na₂CO₃ solution to which some NaOH was added and filtering) was diluted to 5 cc. with water; 1 cc. 30% HAc and then 2 cc. 20% PbAc₂ soln. were added, and the mixtures were heated to boiling and allowed to stand for ten minutes: in the experiments with less than 0.5 mg. ClO, the solutions remained perfectly clear. In that with 0.5 mg. ClO a small, brown precipitate appeared within ten minutes. With 1.0 mg. ClO the brown precipitate was very distinct in one minute, and with 10 mg. it formed while the mixture was being heated.

The experiments were repeated, except that no acetic acid was added: the results were the same, except that small white precipitates of Pb(OH)₂, always formed, and that in experiments with 0.2 and 0.3 mg. ClO these turned brown in 10 or 15 minutes.

The experiments with and without acetic acid were repeated, except that after the addition of the lead acetate the mixtures were allowed to stand at room temperature: in experiments with 50 mg. ClO the brown precipitate formed almost immediately, while with 10 mg. ClO it appeared within 1 to 5 minutes.

Effect of the Presence of Nitric Acid.—The experiments described in the preceding section were repeated, except that 0.5 cc. HNO₃ (1.20) was added instead of acetic acid and 2 cc. 10% Pb(NO₃)₂ solution instead of lead acetate solution: the solutions remained clear and colorless even in the experiment with 50 mg. ClO. These experiments were repeated except that no nitric acid was added: white precipitates of Pb(OH)₂ were formed and turned brown as in the experiments with PbAc₂ in the absence of acetic acid, but the limit of detectability was about 1 mg. ClO.

Solubility of Lead Hypochlorite.—To 10 mg. ClO as NaClO dissolved in 10 cc. slightly alkaline solution were added 2 cc. 20% Pb(Ac)₂ solution; the mixture was shaken and filtered: the white precipitate turned brown on the filter. The filtrate was heated to boiling: a dark brown precipitate formed quickly, and showed the presence of at least 5 mg. ClO in the filtrate. It is to be noted that there is no evidence that any Pb(ClO)₂ precipitated.

Effect of the Presence of Carbonate and of the Absence of Excess of Lead Acetate.—In each experiment a known amount of ClO as NaClO was dissolved in 10 cc. 1% Na₂CO₃ solution in a casserole; 2 to 3 cc. 20% PbAc₂ solution were added, and the mixture was boiled vigorously: the brown color showed at once on heating with 10 mg. ClO, quickly with 2 mg. ClO, and was slight but distinct with 1 mg. ClO; in the last case it became more distinct on vigorous boiling. In some of these cases a portion of the solution was filtered off and Na₂CO₃ added: the formation of a white precipitate showed the presence of lead salt in excess.

The experiment with 10 mg. ClO was repeated, except that only 1 cc. 5% PbAc₂ was added: the test failed. In this and in several other experiments in which the test failed, the solutions were filtered off and shown not to contain lead in excess.

P. 117, N. 3. *Action of Lead Salts on Peroxides and on Hydrogen Peroxide.*—0.1 g. Na₂O₂ was dissolved in 10 cc. water and 2 cc. 20% PbAc₂ solution added: a brown precipitate formed at once, and remained when the mixture was boiled. The experiment was repeated with about 1 mg. Na₂O₂: a brown turbidity appeared at once. The experiment with 1 mg. Na₂O₂ was repeated, except that the PbAc₂ solution was poured

over the dry Na_2O_2 : a dark brown, almost black, precipitate formed at once. The experiment with 1 mg. Na_2O_2 was repeated in the presence of 0.5 cc. 10% Na_2CO_3 solution: the brown color could not be detected in the large white precipitate.

The experiment with 0.1 g. Na_2O_2 was repeated, except that the solution was made slightly acid with acetic acid (the presence of H_2O_2 in the solution was shown by adding a drop of a titanium sulfate solution to a small portion of the mixture): lead acetate solution gave no precipitate even when the mixture was boiled.

To 1 cc. 30% H_2O_2 was added 1 cc. 20% PbAc_2 solution: a brown turbidity appeared, but violent evolution of gas began almost at once and the brown color vanished. On heating the mixture to boiling, no precipitate formed. The experiment was repeated except that 1 drop 30% acetic acid was also added: the solution remained clear at room temperature, but on heating a violent evolution of gas began, and the mixture remained clear and colorless.

P. 118, N. 1. *The Test for Chlorate*.—5 cc. of the H_2SO_4 solution used in the following experiments were equivalent to about 15 cc. of the 4% AgNO_3 solution. Blank experiments were performed in which 10 cc. 4% AgNO_3 solution, 80 cc. water, and known amounts of HNO_3 (1.20) were mixed and 5 cc. H_2SO_4 solution added: a large white precipitate of Ag_2SO_4 formed in the presence of 3 cc. HNO_3 (1.20), but none in the presence of 4 cc. or 5 cc., even on heating to boiling. The experiments were repeated with 10–20 cc. water, instead of 80 cc.: the results were the same.

The experiment with 5 cc. HNO_3 (1.20) in 100 cc. was repeated in the presence of 1 mg. ClO_2 as KClO_2 : within 3 minutes at room temperature the mixture was turbid, and within ten minutes the precipitate was very distinct. This experiment was repeated in the presence of 25 cc. HNO_3 (1.20) instead of 5 cc.: the precipitate of AgCl formed somewhat more quickly than in the experiment with less acid, and was very distinct in less than 3 minutes. The experiment with 5 cc. HNO_3 in 100 cc. was repeated in the presence of 3 mg. ClO_2 as KClO_2 : the precipitate appeared almost at once and increased rapidly in amount.

Reduction of Hypochlorite by Arsenite.—The hypochlorite solution used was that described above in C. E., P. 117, N. 2, and was two weeks old. 100 mg. ClO as NaClO were dissolved in 50 cc. water and 10 cc. HNO_3 (1.20), 10 cc. 10% alkalin Na_2AsO_3 solution were added slowly, and at intervals a few drops of the solution were placed on filter paper moistened with KI solution. Even with this large excess of arsenite a very faint test for iodine was still obtained, doubtless due to the equilibrium, $2\text{HI} + \text{H}_2\text{AsO}_3 = \text{H}_2\text{AsO}_4 + \text{I}_2 + \text{H}_2\text{O}$. AgNO_3 solution was then added in excess, the precipitate filtered off, and the filtrate tested for chlorate by P. 118: a precipitate of AgCl was obtained which was estimated to correspond to 3 to 5 mg. ClO_2 , which amount was probably present in the original NaClO solution.

P. 118, N. 2. *Action of H_2S on AgBr Suspended in Water*.—To 100 mg. Br as freshly precipitated AgBr were added about 70 cc. water and a few drops HNO_3 (1.20), and H_2S was passed into the mixture for 10 or 15 minutes: the white precipitate turned black almost immediately. The liquid was decanted through a filter, and the precipitate was treated repeatedly by the same process, except that in the fourth and fifth treatments the mixture was heated to boiling before filtration. Each filtrate was boiled until the H_2S was expelled, AgNO_3 solution was added, and the amounts of Br extracted by the successive treatments were estimated from the size of the precipitates to be about 50, 20, 10, 15 and 3 mg., respectively. This shows that about half the bromide had been extracted in the first treatment, even in the cold. The experiment was repeated with 1 mg. Br as AgBr : a good test for bromide resulted. A blank experiment was also made, which gave a very satisfactory negative result.

100 mg. Br as freshly precipitated AgBr were suspended in 25 cc. water (not con-

taining any HNO_3), H_2S was passed through for 15 minutes, the mixture heated to boiling, the liquid decanted through a filter, and AgNO_3 added: a precipitate of AgBr resulted which was apparently nearly as large as the amount taken. The residue from the H_2S treatment was washed and heated with HNO_3 (1.20): the residue (of AgBr and S) was less than one-fifth of the amount taken.

P. 119. *Delicacy of the Sulfite and Thiosulfate Tests.*—2 mg. SO_2 as Na_2SO_3 were dissolved in 8 cc. water and 2 cc. 10% Na_2CO_3 ; 3 cc. 10% $\text{Sr}(\text{NO}_3)_2$ solution were added, the mixture was acidified with acetic acid and the clear solution heated to boiling: a finely divided precipitate separated at once. After 15 minutes this was filtered off and treated as described in the Procedure: the precipitate of BaSO_4 was distinct within 5 minutes after adding the bromine. The experiment was repeated twice with 1 mg. SO_2 as Na_2SO_3 : in each case the clear solution became slightly turbid on boiling, and a small but distinct confirmatory test was obtained. The experiment was repeated several times in the absence of sulfite: the solutions remained clear on boiling. In some cases a flocculent precipitate of SrCO_3 formed while the mixture was being heated, but it dissolved on the addition of two or three drops of acetic acid.

Solutions containing 3 mg. S_2O_3 as $\text{Na}_2\text{S}_2\text{O}_3$ in 8 cc. water and 2 cc. 10% Na_2CO_3 were treated as described in the preceding paragraph. To the resulting clear solutions were added 2 cc. HCl (1.20), and the mixtures were heated to boiling and allowed to stand: white precipitates of sulfur usually appeared within half an hour. The experiment was repeated twice with 2 mg. S_2O_3 ; the solutions remained clear for about three hours, but were distinctly turbid in four hours. The experiment was repeated twice with 1 mg. S_2O_3 : the solutions appeared to be nearly clear on standing over night, but became turbid when the mixtures were then shaken and allowed to stand half an hour longer. These experiments were repeated with an excess of 8 cc. HCl (1.20) instead of 2 cc.: in an experiment with 3 mg. S_2O_3 the solution was clear after 1 hour, but became turbid over night, while in the experiments with 2 and 1 mg. no precipitates formed even on standing 24 hours. This shows that a large excess of acid interferes with the test.

To 1 mg. S_2O_3 as $\text{Na}_2\text{S}_2\text{O}_3$ dissolved in 10 cc. water were added 2 cc. HCl (1.12); the mixture was heated to boiling and allowed to stand: there was a small but distinct turbidity in half an hour which increased on standing.

Effect of Excess of Acetic Acid on the Thiosulfate Test.—100 mg. S_2O_3 as $\text{Na}_2\text{S}_2\text{O}_3$ in 8 cc. water and 2 cc. 10% Na_2CO_3 solution were tested for sulfite by the process described in the preceding section: the solution remained clear on boiling. The experiment was repeated, except that an excess of 5 cc. 30% acetic acid was added: the solution became turbid when it was boiled, but the small sulfur precipitate did not increase in amount when the mixture was set aside at room temperature. The experiment was repeated with an excess of only 1 cc. 30% acetic acid: a faint turbidity appeared when the mixture was boiled; the mixture was slightly turbid after 1 hour, but was clear after three hours.

[CONTRIBUTION FROM THE INSTITUTE OF ANIMAL NUTRITION OF THE PENNSYLVANIA STATE COLLEGE.]

ADIABATIC DEVICE FOR BOMB CALORIMETER.

BY J. A. FRIES.

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The value of an adiabatic equipment to a bomb calorimeter lies in the fact that such a device, if only simple enough, may be a means both of saving time and of greater accuracy in determining the heat of com-

bustion. It does away with much tedious computation, and the correct temperature of the calorimeter before and after a combustion is more readily obtained.

Adiabatic devices differing in principles have been described by Richards, Henderson and Trevert,¹ and Benedict and Higgins,² but since these, however valuable in themselves, are not made so as to be easily adjusted to bomb calorimeters that are already installed and in use, a simpler device was sought for to fill that want.

The problem was satisfactorily solved by applying to the bomb calorimeter the same principle which is used in the respiration calorimeter according to Atwater and Rosa. Any bomb calorimeter of the Atwater-Berthelot type can be made adiabatic without much expense by a simple device.

The materials which were used in the construction of the apparatus were such as could be picked up around the laboratory. Hence it is not so much the material as the principle which I want to emphasize.

The following is a description of the arrangement for making the bomb calorimeter adiabatic:

Heating Device.—This consists of a German silver wire about 3.5 meters long and 0.8 mm. in diameter, having a total resistance of about 6.1 ohms. This wire was strung through small brass eyelets screwed directly into the inner insulating fiber jacket of the modified Atwater-Berthelot bomb calorimeter which we are using. The eyelets were so arranged that there was one coil of wire near the bottom a little distance from the sides, the rest of the wire then going up and down along the sides making eight loops spaced as evenly as convenient and coming to within 30 mm. of the top of the inner fiber jacket. The two ends were fastened to insulated copper wire and brought out through the side of the fiber jackets. It was wired in this fashion in order to avoid any induction by the current. Both direct and alternating currents have been tried. At present we use only alternating current. The current which suits this particular wire, or resistance, and which will give the heat needed quickly enough is taken from a 110 volt circuit through five 32 c. p. carbon filament lamps in parallel. The distance between heating wire and fiber vessel is about 6 mm. on the average, leaving 15 to 20 mm. between wire and calorimeter.

With this device alone, however, it was found impossible to measure the true rise in temperature of the air quickly enough by means of mercury thermometers to make possible any use of it in connection with the heat measurements.

Air Thermometer.—Mercury thermometers being found useless for

¹ *Proc. Amer. Acad. Arts and Sci.*, 42, No. 21 (March, 1907).

² *THIS JOURNAL*, 32, 461 (1910).

measuring the air temperature, and electric thermometers being difficult and costly to instal, it was finally decided to use an air thermometer. Besides securing a quick registration of the resulting rise in temperature, it was also necessary to provide some way to regulate the heating effect upon the calorimeter and make it uniform. To use any kind of blower would complicate matters, but the problem was solved by placing the calorimeter inside a double walled copper jacket which constitutes the bulb of the air thermometer.

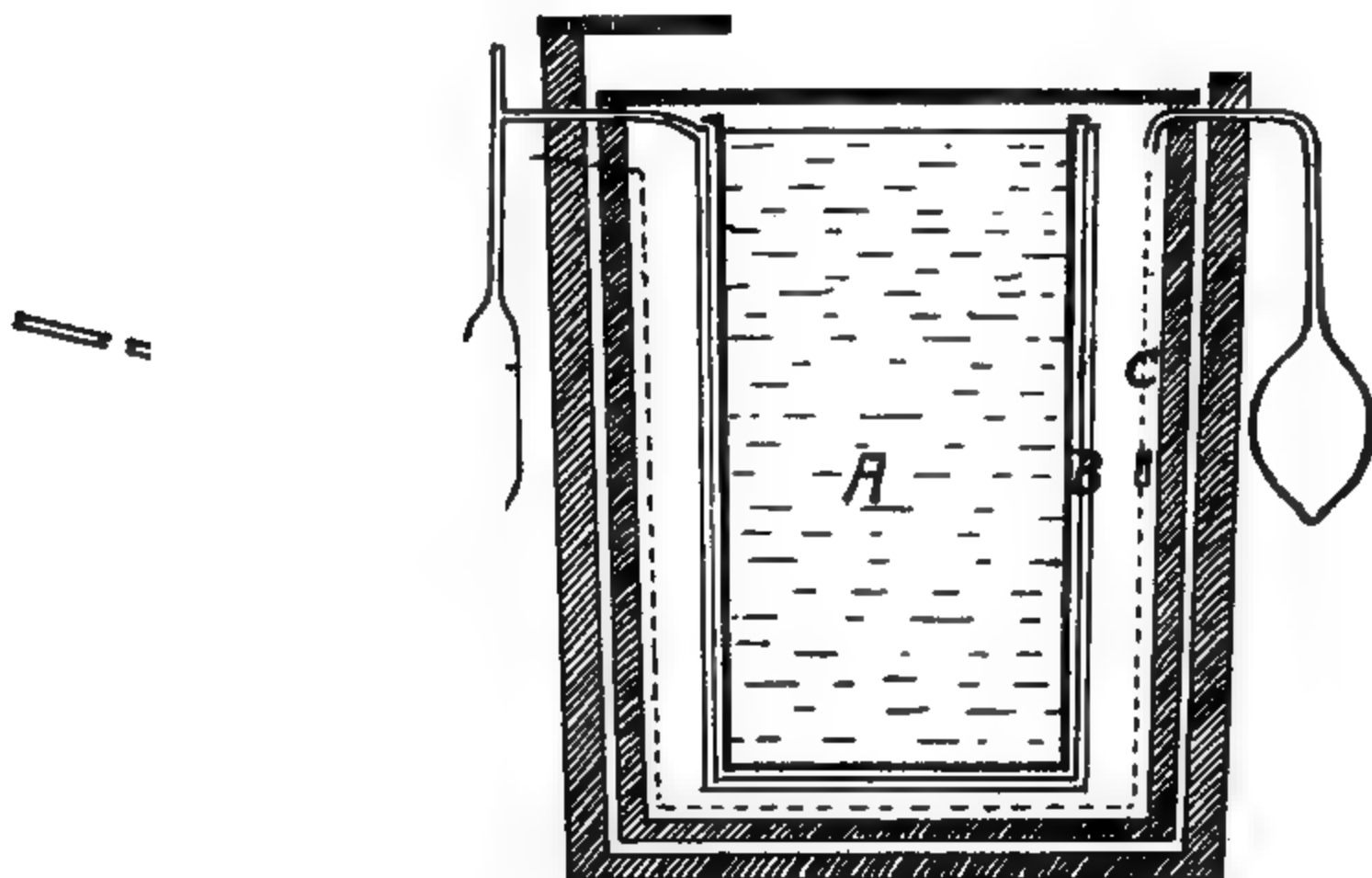
Copper Jacket.—This double walled cylindrical copper jacket was made of polished sheet copper about 0.25 mm. thick and has a 4 mm. air space between the walls and bottoms. In the bottoms there are three holes through which project three screw heads on which the calorimeter rests. The diameter of this jacket is such that when the calorimeter is in place there is an air space of about 4 mm. between the calorimeter and copper at the sides and 5 mm. at the bottom, and the upper edge of the copper is on the same level as the upper edge of the calorimeter. The copper jacket rests on three corks and is held in position by corks at the sides, and the calorimeter is kept in its position within the jacket by means of a few pasteboard blocks glued on the sides of the copper. Care must be taken that the different metals do not touch at any point.¹ At the upper edge a small brass tube is soldered into the copper and connected by good rubber to a piece coming through the fiber walls from the outside. When this air-tight jacket has once been placed in position, it remains as a permanent part of the apparatus.

Tube and Water Reservoir.—The thermometer consists, besides the copper jacket, of a glass tube, bore about 2 mm., which is placed at an angle of about 14 degrees. It is bent in U shape at the end near the jacket and from the bend to the extremity is 85 cm. long. The tube is supported against a fixed strip of wood, which also serves as a support for the calibrated paper scale. Between the brass tube coming from the apparatus and the end of the glass tube, the bulb of a 25 cc. pipet is inserted. This pipet bulb serves as a reservoir for the water (colored with litmus) which serves as the indicating column, and the total water in the system should not be quite sufficient to fill the bulb. This is to prevent the water from being drawn into the jacket should the temperature ever go below the range of the thermometer.

With the copper jacket and tube, as described, one degree change in temperature equals 12.5 cm. on the glass tube. This was considered sensitive enough, although the air thermometer can be made more or

¹ It may be stated that in order to make it convenient to lower the calorimeter filled with water into the copper jacket a depression is made on each side at the upper edge of the jacket so that the fingers can grip conveniently over the edge of the calorimeter when handled.

less sensitive by using a smaller or larger bore tube, or by placing it at a different angle.



A = Calorimeter with water.
B = Double-walled copper jacket.
C = Resistance wire.

Calibration of the Air Thermometer.—This air thermometer is sensitive both to heat and barometric pressure, but since the latter rarely changes materially during the short time required for a heat determination no correction for pressure is necessary.

In order, however, to provide for the use of the full range of the Beckmann thermometer the glass tube must be a little longer than is needed for the given number of degrees, so as to allow for some changes in the atmospheric pressure. Should the barometric pressure change considerably during the day the air thermometer can be adjusted to the existing temperature and pressure conditions in a moment by opening the air valve on the brass pipe just outside the fiber jacket. The amount of water in the tube should be such that when the air valve is open the water column stands a little above the bend of the tube. To prepare the scale representing centigrade degrees a good mercury thermometer on which 0.01° can be estimated by aid of a lens is placed in the copper jacket, the covers are put on, and the apparatus allowed to stand until the conditions have reached constancy. The air valve is then closed, the thermometer lifted up and read and the position of the water column marked.

Heat is then applied by means of the electric current and the water column is kept constant at another point until the mercury thermometer standing in the copper jacket has reached a maximum. This point is marked and the corresponding rise in temperature of the jacket is noted. This operation is repeated until a sufficient number of points have been established to permit the making of the scale which should be graduated at least to 0.1° . If the calibration is extended over considerable periods of time during unsettled weather conditions, the barometric pressure should be noted and corrected for, if necessary.

Being affected by two factors, heat and pressure, a fixed scale is of no value, a movable one must be used, one that can be set to any point within several degrees. In order to have the degrees of equal length upon the tube, care must be taken in selecting one having a uniform bore.

Sensitiveness.—The long space on the scale equal to a tenth of a degree makes it easy to estimate to a hundredth of a degree by the naked eye at some little distance away. The heating effect of the electric current, previously referred to, may be seen from the following table which gives the time of the current in seconds, and the rise in temperature of the air thermometer at different intervals. These results may vary somewhat with the temperature condition of fiber jackets and surrounding air, as well as with changes in voltage.

TABLE I.

Rise in temperature in

Current in seconds.	30 seconds. °C.	1 minute. °C.	Total. °C.
20	0.28	0.58	0.76
25	0.35	0.78	1.05
30	0.52	0.95	1.35
35	0.52	1.17	1.63
40	0.52	1.37	1.81
45	0.52	1.58	2.00

In about $1\frac{1}{2}$ minutes after the current is off, the water column has practically ceased to rise and in 3 to 4 minutes the maximum rise is reached. Here it remains constant for some minutes before it begins to fall again, so that unless one wishes to take the readings of the calorimeter temperature for a longer period than 3 or 4 minutes after the maximum has been reached, it is not necessary to hold the temperature of the air thermometer constant by further short contacts.

When a charge is ignited in the bomb, the Beckmann thermometer will begin to show a rise in 10 seconds, increasing so that the most rapid rise is between 30 and 60 seconds after ignition. In 30 seconds after ignition of a substance in the bomb the heat from the calorimeter is beginning to show on the air thermometer.

The air thermometer begins to show the effect of the heating current in less than 8 seconds, and sooner when the air between copper and fiber jacket is stirred by means of a rubber bulb. The effect which this heating has upon the calorimeter may be seen from the following observations, giving the change in calorimeter temperature per minute which took place during a given period of time with a given difference between the average of the air and calorimeter thermometers.

During these tests the calorimeter contained the bomb and 2000 grams of water, which was stirred as during a heat determination.

TABLE II.—TEMPERATURE VARIATIONS IN CALORIMETER DUE TO DIFFERENCE BETWEEN ITS TEMPERATURE AND THE SURROUNDING AIR TEMPERATURE.

Minutes.	Temperature of calorimeter water.	Average of air thermometer.	Difference.	Change in calorimeter temperature per minute.
1st to 4th	24.182°	24.40°	0.22°	0°
5th to 11th	24.190	24.97	0.78	+0.0025
12th to 16th	24.207	25.25	1.04	+0.0035
1st to 9th	24.086	23.96	—0.13	—0.0008
10th to 13th	24.080	24.00	—0.08	—0.0004
1st to 5th	26.040	25.20	—0.84	—0.0050
6th to 8th	26.023	25.73	—0.29	—0.0035
9th to 14th	26.017	25.96	—0.06	—0.0008

In these short tests the temperature of the calorimeter was about 0.5° above that of the fiber jackets in the case of the first five, and about 2.5° above in the last three.

From the foregoing figures we see that with the air thermometer 0.22° above that of the calorimeter no change was observed in the calorimeter temperature during four minutes. When heat was applied so that the air thermometer registered 0.78° on an average more than the calorimeter temperature there was a rise of 0.0025° per minute, etc. On the other hand we see a drop in the temperature of the calorimeter when the air thermometer was allowed to fall below that of the calorimeter. At the upper limit of the scale and with the abnormally great difference in temperature between the calorimeter and fiber jackets the drop in the calorimeter temperature was relatively somewhat greater than in the first cases.

Tests of the Apparatus.—The purpose of the adiabatic device is to prevent loss of heat from the calorimeter when its temperature is raised above that of the surrounding media during a determination. A test, therefore, of the efficiency of the arrangement would be to be able, by the use of it, to hold the calorimeter temperature constant when it is higher than the room temperature and that of the rest of the apparatus.

Of the three tests of longer duration given below, one (a) was made near the upper limit of the scale, with a difference of about 1.5° between the calorimeter and the rest of the apparatus. In another trial (b),

near the lower limit of the scale, there was a difference of about 0.5° between the calorimeter contents and the fiber jackets and covers. A third trial (c) is given in which the temperature of the bomb contents was adjusted practically to that of the room and the rest of the apparatus. In this case no heat was applied, the water being stirred as in a determination of heat of combustion. Under these conditions there should be no change in the temperature anywhere. Having no automatic heat regulator in the room, perfect test conditions could not be obtained but they were sufficiently so for our purpose.

TABLE III.

Minutes.	(a)		(b)		(c)	
	Calorimeter temperature.	Air thermometer.	Calorimeter temperature.	Air thermometer.	Calorimeter temperature.	Air thermometer.
1st	25.189 $^{\circ}$	25.35 $^{\circ}$	21.358 $^{\circ}$	21.47	21.491 $^{\circ}$	21.48 $^{\circ}$
3rd	25.189	25.34	21.358	21.47	21.491	21.48
5th	25.189	25.34	21.358	21.47	21.491	21.49
7th	25.189	25.34	21.358	21.47	21.491	21.49
9th	25.190	25.33	21.359	21.47	21.491	21.49
11th	25.190	25.30	21.358	21.44	21.492	21.49
13th	25.190	25.29	21.357	21.46	21.492	21.49
15th	25.190	25.29	21.357	21.46	21.493	21.49
17th	25.190	25.28	21.357	21.47	21.493	21.49
19th	21.357	21.48
21st	21.357	21.49
24th	21.357	21.50

In (a) and (b) of the above tests the calorimeter and its contents were warmer than the rest of the apparatus when placed in position. After being placed in position and the stirrer started the heat was applied gradually until the air thermometer registered as noted in the table.

At the beginning of test (a) when the air thermometer registered 0.16° above that of the calorimeter the temperature of the latter remained constant for 5 minutes. After that there was a tendency of the calorimeter temperature to rise, but it remained constant when the difference in temperature was gradually falling, until at the end of the test it was but 0.10° . With a difference of 0.11° in the beginning of test (b) the temperature of the calorimeter remained constant for 9 minutes. Only a slight cooling of the air caused a drop in the calorimeter temperature, but with a difference of 0.13° the temperature again remained constant.

The fact that it is necessary to have the air thermometer read 0.10 – 0.16° higher than the calorimeter in order to keep the latter at a constant temperature may be ascribed to the fact that there is a constant radiation of heat from the water surface and top of the calorimeter to the colder air and covers. It being impracticable to extend the copper jacket over the top, extra heat must be supplied through the sides and bottom of

the calorimeter to compensate for the loss of heat at the top and keep the whole system in equilibrium.

This necessary difference in temperature will no doubt vary with each instrument while, as the foregoing results show, and as would be expected, it is greater the greater the excess of the calorimeter temperature is over that of the surroundings. When working under uniform conditions, a little experience will soon show what excess is necessary.

In test (c) of Table III, no heat was applied, but the water in the calorimeter was stirred as during the other tests. After the fourth minute the air thermometer remained constant, but the calorimeter temperature rose 0.002° in 17 minutes. This slight rise in the calorimeter temperature can only be ascribed to one of two causes. It must either be due to heat generated by the stirrer or else due to increase in barometric pressure affecting the reading of the air thermometer. The writer inclines to the latter explanation, although during these tests the weather was rainy and, hence, there is a possibility that the heat produced by friction of the stirrer may have exceeded the loss of heat due to evaporation of water, which under ordinary winter conditions, judging from common observations only, appears to exceed that produced by friction of the stirrer.

Rise in Temperature Due to Combustion.—For the particular bomb calorimeter in question the rise in temperature due to a definite number of calories generated in the bomb may be seen in the following table:

TABLE IV.—RISE IN CALORIMETER TEMPERATURE WHEN HEAT IS GENERATED IN THE BOMB.

Heat generated. Calories.	Rise first minute.	Total rise.
5000	1.60°	2.06°
4500	1.35	1.86
4000	1.10	1.65
2000	0.56	0.80

The rise in temperature during the first minute may vary slightly according to the nature of the substance ignited.

Manipulation.—While the bomb is gotten ready for a determination, both covers of the apparatus are kept in position and a good mercury thermometer is allowed to stand in the copper jacket. When the bomb has been charged with oxygen, and the necessary amount of water, a little warmer than the apparatus, has been put in the calorimeter, the air valve is closed, the temperature of the air in the apparatus is taken, and the scale set so that the end of the water column will indicate that temperature. The covers are now removed, calorimeter and bomb placed in position and stirrer started. After a couple of minutes raise the air thermometer readings, by making short contacts, to 0.10° to 0.15° above the reading of the Beckmann thermometer in the calorimeter

water. Take a reading or two to be sure that the calorimeter temperature remains constant. Ignite the charge and at the same time close the switch on the heating circuit.

The length of time during which the current should be on depends upon the amount of heat generated in the bomb. If, for instance, we expect about 4500 calories, a glance at Table IV shows that the total rise in temperature will be 1.86° and about 1.35° at the end of the first minute. From Table I we see that the current on for 40 seconds with perhaps one or two additional short contacts will meet the conditions. Whether the total current should be on continuously for that length of time, or whether under any conditions it would be of advantage to make shorter contacts with some seconds of time between, experience will soon decide.

Readings of the thermometers are taken as usual every minute. The maximum temperature will be obtained in from 3 to 5 minutes according to the charge. In most cases 4 minutes decides the maximum rise, but a couple more readings should be taken to make sure that the temperature is constant.

Computation.—The computations are much simplified by this method of determination. Only the reading of the Beckmann thermometer taken at the time of ignition and the maximum reading after ignition, usually at the fourth minute, receive the thermometer corrections. The true temperature difference is multiplied by the water equivalent of the apparatus, and from this product is subtracted the heat due to the iron wire or other material used for ignition and the acid formed during the combustion.

Cooling the Apparatus for the Next Determination.—As determinations are usually made with the bomb calorimeter, considerable time elapses between the ignitions, and the copper jacket and air wall acquire the room temperature without any further attention. To hasten the lowering of the temperature, a small toy fan, 5 inches in diameter, and driven by 2 to 3 dry batteries, can be placed above the apparatus for a few minutes, or a beaker or other vessel with cold water may be set down in the copper jacket for a little while. The covers are then put on, the mercury thermometer replaced and the apparatus allowed to stand to be ready for the next determination.

Energy Determinations Influenced by Air Temperature.—The following table gives the difference in temperature between the calorimeter and the surrounding air space at different times during the determination and also the results obtained for the heat of combustion of benzoic acid.

These four determinations show a range of air temperature conditions within which it is easy to keep the apparatus and the results come practically within the limit of analytical error, the theoretical value of benzoic

TABLE V.—AIR TEMPERATURE ABOVE OR BELOW THE CALORIMETER TEMPERATURE.

At time of ignition. ° C.	1 minute after ignition. ° C.	Average during 4 minutes. ° C.	Calories per gram ben- zoic acid.
+0.34	—0.25	+0.13	6323.0
+0.11	—0.15	+0.01	6315.0
+0.16	+0.05	+0.16	6316.3
+0.13	—0.25	+0.13	6323.3

acid being 6320 calories according to the U. S. Bureau of Standards. These results show that the adiabatic arrangement is very sensitive and capable of giving very good results.

STATE COLLEGE, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
**A STUDY OF COBALTNITRITES AND THEIR APPLICATION TO
 ANALYTICAL CHEMISTRY.**

BY LAURIE LORNE BURGESS AND OLIVER KAMM.

Received March 5, 1912.

A. Silver-Potassium Cobaltinitrites: A New Qualitative Test for Potassium.

The quantitative determination of the alkali metals has long been one of the most troublesome of analytical problems. In 1900, Adie and Wood¹ demonstrated the possibility of employing the cobaltinitrite method for potassium as a rapid and accurate volumetric process, and since that time much work has been done to bring it to perfection. The solution of this problem is of prime importance to agricultural chemists and consequently the activity in this field has been confined mainly to them. Notwithstanding a good deal of careful work, results obtained have proven far from satisfactory. For this reason we have undertaken a rather extensive theoretical study of the subject, hoping to overcome the difficulties now encountered in its application to analytical work. Our method of attack has been from the physico-chemical standpoint, for we believe that this problem will be solved only after having obtained a proper knowledge of the behavior of these complex substances when in solution. It was during the course of such an investigation that a series of new compounds was prepared, and it is the purpose of this article to recommend one of them as a new qualitative test for potassium.

In this preliminary paper we do not intend to give a historical review of the subject. It may be necessary, however, to mention the work of Drushel,² Bowser,³ and Shedd,⁴ all of whom have attempted to apply the dipotassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, to the quantitative

¹ *J. Chem. Soc.*, 77, 1076 (1900).

² *Am. J. Sci.*, 24, 433 (1907); 26, 329; 26, 555 (1908); *Chem. News*, 97, 124 (1908).

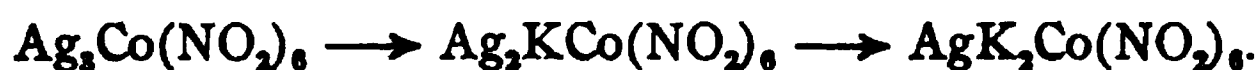
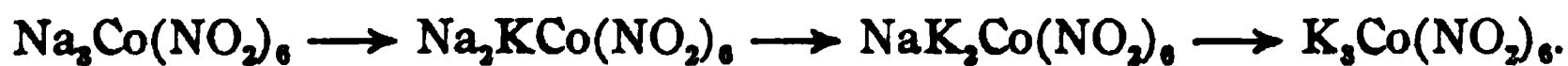
³ *J. Ind. Eng. Chem.*, 1, 791 (1909); *Chem. News*, 101, 100 (1910); *THIS JOURNAL*, 32, 78 (1910).

⁴ *J. Ind. Eng. Chem.*, 1, 302 (1909); 2, 379 (1910).

determination of potassium. The use of the same reaction as a qualitative test will be found described in most text-books on "Qualitative Analysis." Bray¹ has shown that the test is delicate enough to detect sixty parts of potassium per million, provided a large excess of reagent is used. Recently, Bowser² has increased its sensitiveness by precipitating in the presence of ethyl alcohol. A similar reaction, depending upon the formation of the tripotassium salt, $K_3Co(NO_2)_6$, is commonly used in the analytical laboratory for the detection of cobalt in the presence of nickel. As little as two parts of cobalt per million may be detected in this way. The method was originally proposed by Fischer³ in 1848.

The reagent used in these qualitative tests is a solution of the sodium salt, $Na_3Co(NO_2)_6$, which may be prepared as described by Adie and Wood.⁴ We have found it preferable, however, to use a solution of the pure substance, thus eliminating the large excess of sodium and cobaltous salts as well as acetic acid which, as will be shown later, interfere with the sensitiveness of the reagent. The pure sodium salt may be prepared by precipitation with ethyl alcohol as described by Cunningham and Perkin.⁵ In the following experiments we have used a freshly prepared 25% solution of pure sodium cobaltinitrite.

When a drop of this reagent is added to a solution containing 1% of potassium, a yellow precipitate is formed immediately, which consists of tripotassium cobaltinitrite, $K_3Co(NO_2)_6$, or of the dipotassium salt, $K_2NaCo(NO_2)_6$, according to the amount of reagent used.⁶ In the presence of silver ion, however, the corresponding silver salts are formed. The entire series is represented here.



It would appear that as we replace sodium in the trisodium salt with potassium, we obtain less soluble substances. In the same manner if we replace sodium in the sodium-potassium derivatives, with silver, we obtain even less soluble salts—the silver-potassium cobaltinitrites. The delicacy of the latter reaction is shown by the following experiment: A drop of reagent added to a very dilute solution of potassium (less than 100 parts per million) produces no perceptible precipitate. If the test is repeated in the presence of 0.01 *N* silver nitrate, a copious yellow precipitate is formed immediately. In the absence of potassium nitrate but using the same concentration of silver as before, it is found that the

¹ THIS JOURNAL, 31, 613–621–633 (1909).

² *Ibid.*, 33, 1566, 1752 (1911).

³ *Pogg. Ann.*, 74, 124 (1848).

⁴ *Loc. cit.*

⁵ *J. Chem. Soc.*, 95, 1562 (1909).

⁶ *Ibid.* (See also Gilbert, "Inaugural Dissertation," Tübingen, 1898.)

trisilver and the silver-sodium salts are not precipitated. Because of this fact it is possible to use these silver-potassium cobaltinitrites as a delicate qualitative reaction for potassium. In applying the test, it is essential that the solution be neutral or only slightly acidified with acetic acid. Halogens may be removed by the addition of silver nitrate, a large enough excess being added so as to obtain approximately a 0.01 *N* solution. Interference due to the presence of other substances is discussed below.

In the usual scheme of analysis the test may be applied after the removal of the heavy metals. The filtrate from the latter is acidified with an excess of nitric acid, evaporated to dryness and the ammonium salts volatilized. The residue is extracted with water and the solution tested for potassium in the manner already described.

The silver-potassium cobaltinitrite precipitate is very insoluble, in fact, it serves to detect even less than one part of potassium per million. It comes down in a very finely divided condition, and examination under the microscope shows it to be amorphous. It exhibits a marked tendency to pass into the colloidal condition when washed with pure water but is coagulated by solutions of electrolytes. Alcohol serves the same purpose. The color of the precipitate varies from yellow to orange according to the conditions of the precipitation. Its composition also appears to be dependent upon these conditions; the larger the excess of silver present in the original solution the more will be found in the precipitate. There is also a slight tendency for sodium to be carried down; the nature and extent of this contamination is under investigation at the present time.

The delicacy of this qualitative test for potassium is shown by the following table. The fourth column represents approximately the time required for the decomposition of the precipitate, a phenomenon which accounts for the varying results obtained when determining the solubility of any cobaltinitrite. As would be expected, the precipitate is more stable in the presence of an increased volume of reagent.

TABLE I.

Parts potassium per million.	Vol. $\text{Na}_2\text{Co}(\text{NO}_2)_6$ used.	Precipitate appeared after,	Precipitate lasted.
3.0	1 drop	almost immediate	60 min.
2.0	1 drop	almost immediate	30 min.
1.0	1 drop	15 sec.	5 min.
0.5	0.5 cc.	2 min.	30 min.
0.2	1.0 cc.	turbidity after a few min.	

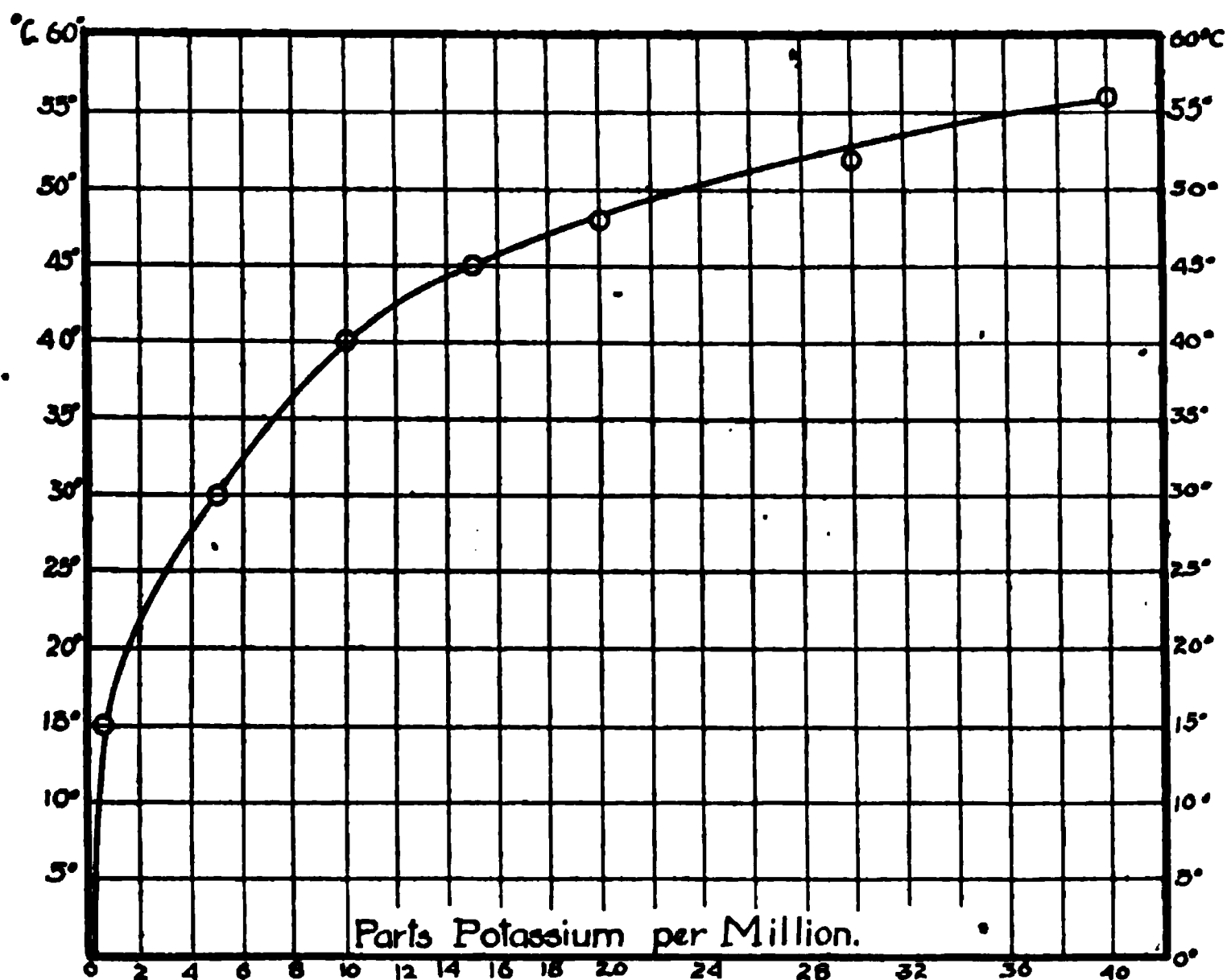
All of the above tests were made at a temperature of 15°, and the same concentration of silver nitrate (0.01 *N*) was used in every case.

It is thus seen that the silver-potassium cobaltinitrite precipitate serves as an extremely delicate qualitative reaction for potassium. Its ad-

vantages over the old method are: (1) It is more sensitive.¹ (2) The test may be made with the use of a single drop of reagent added to 100 cc. of the solution.

When a mere trace of potassium is to be detected, the temperature of the solution must be considered, because of the rapid decomposition of the complex ion, $\text{Co}(\text{NO}_2)_6^{--}$. The latter is very unstable in dilute solutions and its rate of decomposition increases rapidly with increasing temperature. For example, at 15° we may detect one-half part of potassium per million. At a temperature of 30° , however, the limit of sensitiveness is five parts per million, while above 40° no precipitate is obtained with ten parts, a single drop of reagent being used in each case.

The results of a series of experiments of this kind have been plotted, using the temperature as ordinate and the concentration of potassium as abscissa. The curve obtained represents graphically the effect of increasing temperature upon the delicacy of the test. The points on the curve represent the temperatures at which a known amount of potassium will just fail to produce a precipitate, the concentration of silver nitrate being 0.01 N. With the use of this curve we may make an approximate analysis of a solution containing potassium, by observing the temperature at which a temporary precipitate is formed. Only a few drops of



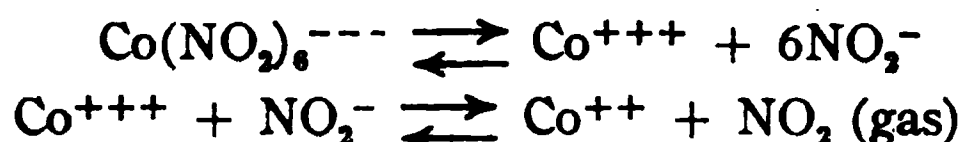
¹ Although Bowser's modification is delicate enough to detect two parts of potassium per million, it possesses a distinct disadvantage in that no definite precipitate, but only a temporary turbidity, is formed in such dilute solutions.

reagent are added in order to avoid an excessive amount of sodium nitrite whose presence will interfere with the delicacy of the test. The explanation for this is given above.

The only substances interfering with this qualitative reaction for potassium are those that also interfere with the usual test in which the tripotassium salt is formed. Ammonia should be absent because it forms not only a triammonium salt¹ but also a less soluble salt containing silver. Rubidium, cesium, thallium, lead, and mercurous salts also interfere, as will be shown below. Barium forms sparingly soluble cobaltinitrites but the other alkaline earth metals do not. In concentrations below 0.1 *N*, barium will not interfere under the usual conditions.

In the dilute solutions used, sodium salts will not appreciably affect the delicacy of the test. When only a trace of potassium occurs in the presence of a tenth normal solution of sodium, the precipitate forms more slowly than usual, and it may be necessary to add a larger volume of reagent in order to secure complete precipitation. An increase in the amount of silver increases the delicacy of the test. Thus, any effect which is due to sodium may be counteracted by increasing the concentration of the silver. It is only when dealing with very dilute solutions of potassium, *i. e.*, ten parts per million or less, that the effect of the sodium or of the silver ion need be considered.

In general, an excess of reagent increases the sensitiveness of the test provided that there has been no decomposition of the cobaltinitrite. This decomposition takes place in accordance with the following reactions, resulting in the increase in the concentration of nitrite ion.



The effect of the presence of a soluble nitrite, such as sodium nitrite, is to prevent the complete precipitation of the potassium. This is explained by the formation of the complex ion, $\text{Ag}(\text{NO}_2)_x$, with a consequent decrease in the concentration of silver ion. We have found that a certain definite concentration of the latter must be present in order to precipitate the silver-potassium salt from a solution containing a given concentration of potassium. Since the addition of a nitrite removes silver ion from solution, we can, by adding a sufficiently large amount of the former, decrease the concentration of the latter to such an extent that the silver-potassium salt will fail to be precipitated.

The following experiment will illustrate this point: When a drop of reagent is added to a 0.01 *N* solution of silver nitrate containing ten parts of potassium per million, an immediate precipitate is formed. If, however, the experiment is repeated in the presence of a 0.1 *N* solution

¹ Erdmann, *J. prakt. Chem.*, 97, 404 (1866). Rosenheim and Koppel, *Z. anorg. Chem.*, 17, 35 (1898).

of sodium nitrite no immediate precipitate is obtained under the same conditions, *i. e.*, we have decreased the concentration of the silver ion to such a small value that not enough is present to produce a precipitate. If a larger amount of potassium is present, or if an increased volume of reagent is added, a precipitate will be obtained. This is exactly what the law of mass action would lead us to expect.

Another interesting point may be brought out here. The silver-cesium salt mentioned below is less soluble than the corresponding potassium salt. We would, therefore, expect it to be precipitated by a smaller concentration of silver ion than is needed to precipitate the potassium salt. This was actually found to be the case, *i. e.*, when enough sodium nitrite was added to prevent the precipitation of the potassium salt, an equivalent amount of cesium, rubidium or thallium was still precipitated because of the smaller concentration of silver ion necessary.

It may be suggested that the silver-potassium cobaltinitrites could be used as a delicate qualitative test for cobalt. They do not, however, offer any distinct advantage. The usual reaction, *i. e.*, the formation of $K_3Co(NO_2)_6$, is very sensitive, due to the large concentration of potassium salts which decreases the solubility of the precipitate.

B. Other Insoluble Salts in this Series.

The fact that potassium forms extremely insoluble cobaltinitrites led us to believe that other alkali metals would form similar silver salts. Considering the series Li, Na, K, Rb and Cs, in which the elements are arranged in the order of increasing atomic weights, we find that the lithium and sodium salts are very soluble while the potassium salts are rather insoluble. We would, therefore, expect the rubidium and cesium cobaltinitrites to be even less soluble, and Rosenblatt¹ has shown that this is the case. The following table shows the concentrations at which no precipitate was obtained when one drop of reagent was used. The results are, of course, only comparative, the test being more delicate when a larger volume of reagent is used.

TABLE II.

Concentration necessary for precipitation.

K	100 to 150 parts per million
Rb	70 to 80 parts per million
Cs	70 to 80 parts per million
Tl	30 to 50 parts per million

Rubidium, cesium and thallium also form insoluble silver salts. Solutions of their salts so dilute that the reagent itself gives no precipitate readily form the characteristic insoluble yellow silver cobaltinitrites when in the presence of 0.01 *N* silver nitrate. They are all less soluble than the corresponding silver-potassium salts, and like the latter may

¹ *Ber.*, 19, 2531 (1886).

readily be precipitated from solutions containing less than one part per million (temp. 15°C.).

Ammonium salts also form an insoluble silver-ammonium cobaltinitrite. The latter may be precipitated from solutions containing less than five parts of ammonia per million. This would serve as a delicate qualitative test for ammonia in the absence of potassium.

Silver, lead, and mercurous mercury all form cobaltinitrites. Of these the silver salt, $\text{Ag}_3\text{Co}(\text{NO}_2)_6$,¹ and the lead salt, $\text{Pb}_3[\text{Co}(\text{NO}_2)_6]_2$,² have been described in the literature, but we have not been able to find any reference to their double salts with the alkali metals. The mercurous cobaltinitrite, probably $\text{Hg}_3\text{Co}(\text{NO}_2)_6$, has not, as far as we know, been described. It appears to be the least soluble of all the simple salts of the cobaltinitrite series.

Some of the double salts in the lead series are the lead-ammonium, the lead-potassium, the lead-rubidium, the lead-caesium and the lead-thallium salts. All of them are more soluble than the corresponding silver derivatives, but are less soluble than are the simple cobaltinitrites. It may be interesting to note here that we have also prepared a lead-silver cobaltinitrite, which apparently stands intermediate between the lead and the silver series. It is less soluble than either the silver or the lead salt.

Rosenheim and Koppel³ have prepared the barium salt, $\text{Ba}_3[\text{Co}(\text{NO}_2)_6]_2$. We have found that barium also forms a barium-silver salt. It is less soluble than the simple barium salt and may be precipitated from a tenth normal solution of barium provided the concentration of silver is more than 0.01 *N*. It decomposes more readily than any of the other cobaltinitrites studied.

The barium and lead salts mentioned above are very sensitive to the conditions of the precipitation, and their study may be of importance from this standpoint. They are crystalline in nature.

Cunningham and Perkin⁴ have described certain cobaltinitrites containing organic radicles, such as the anilincobaltinitrite, $(\text{C}_6\text{H}_5\text{NH}_2)_3\text{Co}(\text{NO}_2)_6$. We have found the corresponding silver salts to be less soluble.

Summary.

1. New silver-potassium cobaltinitrites are described.
2. They are recommended as a delicate qualitative reaction for potassium. Directions for applying the test, its delicacy, and all interferences have been given in detail.
3. The corresponding silver salts with ammonium, rubidium, caesium,

¹ Cunningham and Perkin, *loc. cit.*

² Rosenheim and Koppel, *loc. cit.*

³ *Loc. cit.*

thallium and lead are mentioned, and the possible use of some of them in analytical work, indicated.

4. A corresponding series of double salts with lead and the alkali metals has been prepared.

In conclusion we wish to state that we are continuing the study of cobaltinitrites and their application to analytical work—particularly the application of the silver-potassium cobaltinitrites to the quantitative determination of potassium.

A COLORIMETER FOR RAPID WORK WITH WIDELY VARYING STANDARDS.

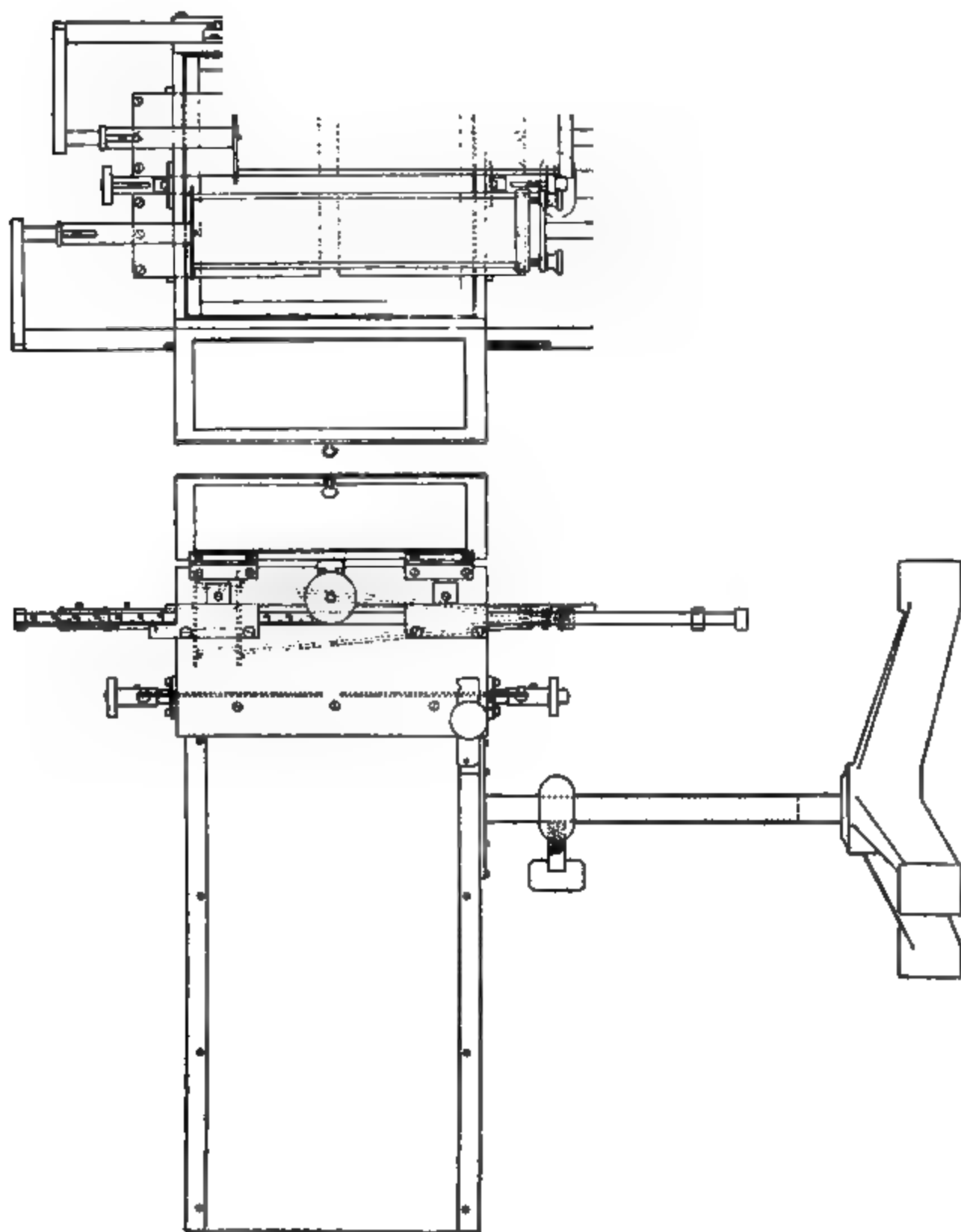
BY CHARLES H. WHITE.

The intensity of the color of a solution depends upon three elements, or factors. They are the quantity of coloring matter used, the volume of the solvent in which it is held, and the thickness of the solution through which the light passes before entering the eye. It is well known that if we keep two of these quantities constant and vary the third in a determinate way until two solutions are alike in color, we can estimate the quantity of coloring matter in one, if the quantity in the other is known. These three variables form the basis of the three classes of methods in colorimetry, and of the three types of colorimeters. When two solutions are brought to agreement in color by the addition of coloring matter to one, the amount added is the measure of that in the other. If the agreement is effected by dilution, the coloring matter is then proportional to the volumes. If they are brought to equality by changing the thickness of the sections observed, the quantity of coloring matter is then inversely proportional to the measurements of these sections.

This instrument is a modification of a colorimeter devised by the writer for the determination of carbon in steel.¹ With it comparisons are made by the third method; that is, the thickness of the section of solution examined is the variable. It consists essentially of two wedge-shaped hollow glass prisms of exactly equal dimensions and open at the large end for the introduction of the solutions to be tested. The wedges are held in a vertical position side by side in a camera and may be raised or lowered by rack and pinion actuated by thumb screws. The prisms are screened from view on the side towards the operator except for a narrow horizontal slit across the middle of the camera through which the solutions are observed when a test is being made. The carriers are graduated to correspond to the length of the wedges, the zero of the scale being opposite the index when the sharp edge of the wedge is opposite the narrow opening in the screen through which the color is observed. The screens are

¹ *Trans. Am. Inst. Min. Eng.*, 38, 559-564.

adjustable so that the opening may be varied to suit the operator. The ground glass shutter at the forward end of the camera for diffusing the light is hinged in the manner of a door to facilitate the transfer of the wedges to and from the camera. The camera is mounted on a stand upon which it is free to turn in a horizontal plane, which renders it unnecessary to lift the instrument from its position while in use.



To carry out a determination with this instrument it is only necessary to dissolve and dilute to equal volumes equal quantities of the standard

and of the material to be tested. Pour into the wedges convenient amounts of the two solutions, set the wedge containing the unknown at the graduation representing the percentage—or some multiple of it—of the coloring matter in the standard. Adjust the wedge containing the standard until the two agree in color. The percentage of coloring matter in the unknown is then indicated by the reading of the scale on the carrier containing the standard. Vertical sections through the two solutions parallel with the line of sight are similar triangles, the base of each being the thickness of solution at the point compared. It follows then that the readings on the graduated scales, since they represent the altitudes of these triangles, are measures which express the ratio existing between the amounts of coloring matter in the two solutions.

A colorimeter for general use, especially where a great many determinations have to be made in the shortest possible time, should be designed with not only the theoretical perfection of the instrument itself in mind, but also with regard to the effect of its use upon the operator. The operation of the instrument must not unduly fatigue the eye, for the most skilled operator with the best apparatus cannot produce accurate results if his eye loses its sensitiveness to changes of color. It has been learned by experience that the eye is little fatigued and therefore retains its sensitiveness if the apparatus is so constructed that both eyes are used in making the tests, also that the eyes should be protected by a camera from side lights, that the colored areas compared should not be too far apart—though it is unnecessary to have them separated only by an invisible line—and that uniform white light should be visible around the colored spots compared. My experience has indicated that the eye is not rendered sensitive to color by darkness, but that it is rendered so by light, and I have obtained better results by looking directly at the solutions than by bringing the colors into juxtaposition by the use of any optical device that I have tried so far.

As a result of experience, the original design of this instrument has been modified to conform to these ideas. In its present form the instrument has been tested, chiefly in the determination of carbon in steel, and these tests indicate that it has several features to recommend it. The accuracy of the work done with it appears to be limited only by the sensitivity of the eye to color changes. The maximum error, as far as tests have been made, has been 0.6% in a single reading, and this was considerably reduced by averaging several readings. The majority of the determinations of carbon have agreed with the percentages obtained by combustion to the second decimal place. The comparisons are made with great rapidity. After the material is in solution the test can be completed within half a minute, and any number of readings may be taken and the results averaged without changing the volume of the

solutions. The operator can not see the graduated scales while making the comparison and, therefore, can not be influenced by preconceived ideas. The work may be checked by making tests at different points throughout the length of the wedges, especially in cases where the color is too dense or too faint for the most accurate comparison at the first point tested.

The wedges are as easily emptied and filled as test tubes so that passing from one determination to the next is quickly and easily effected. If great rapidity is desired more than one set of wedges can be used. While one operator makes the comparisons, others can be preparing the determinations which are to follow. The possibility of using any section of the wedge from its thinnest to its thickest part renders the apparatus adaptable to a wide range of determinations, and permits of much variation in the quantity of substance taken for the test.

The colorimeter is sold by Eimer and Amend of New York City.

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NOTES.

A Modification of a Previously Described Experiment on the Migration of Ions.—A lecture experiment illustrating the rates of migration of different ions was described some years ago by Noyes and Blanchard.¹ Unless this experiment is very carefully performed, it sometimes happens that the demonstration of the direction and relative speed of migration of the copper, hydrogen and hydroxyl ions is rendered inconclusive by the

uneven front presented by the line of march. There frequently happens an irregular diffusion downward into spaces between the agar-agar and the walls of the U tube.

¹ THIS JOURNAL, 22, 726 (1900).

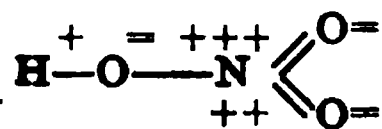
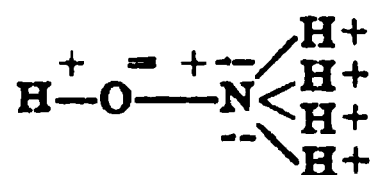
This may be prevented and the experiment more simply and successfully performed in the following manner: Add one part of agar-agar to about five parts of boiling water, and after solution add potassium chloride, phenolphthalein and sufficient potassium hydroxide to color the solution pink. Completely fill a U tube with the mixture and by means of a pipet containing dilute hydrochloric acid passed to the bottom of one limb, discharge the pink color by allowing a small amount of the acid to escape and by stirring the mixture with the pipet as it is withdrawn. After congelment insert the pink limb of the inverted tube into a small bottle containing a solution of copper chloride and dilute hydrochloric acid, and the other limb into a bottle containing a solution of potassium chloride and potassium hydroxide, slightly inclining the tube, if necessary, to allow any entrapped air bubbles to escape.

Upon the application of the current in the usual way the migration proceeds in an orderly manner, and no skirmishers are sent on ahead. The process may proceed for days, if desired, and no cooling is necessary.

E. E. CHANDLER.

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A Possible Explanation of Some Phenomena of Ionization by the Electron Theory.—Many chemists must have noticed the curious fact that ammonium hydroxide, $\text{H}-\text{O}-\text{NH}_4$, and nitric acid, $\text{H}-\text{O}-\text{NO}_2$, ionize, the first with the formation of hydroxide and the second with the formation of hydrogen ions, although in both cases a hydroxyl group is supposed to be combined directly with a nitrogen atom. The statement has, of course, been made that this is because the ammonium, NH_4 , group is positive and the nitro, NO_2 , group negative but these terms, "positive" and "negative," have been used in a very vague way, and with almost no thought of any genuine electrical properties. A possible explanation becomes apparent if we write the two formulas as follows, in accordance with the electron theory:



In ammonium hydroxide the nitrogen atom with its three extra electrons (it has gained four from the hydrogen atoms but has lost one to the oxygen atom) attracts the negative oxygen of the hydroxyl only feebly, hence, the group may easily separate by ionization. In nitric acid, on the other hand, the nitrogen atom has lost five electrons, becoming strongly positive. It holds the negative oxygen atom very strongly, therefore, but repels the positive hydrogen, causing this to ionize easily.

For the compounds $\text{Na}^+ - \text{O}^- - \text{H}^+$ and $\text{H}^+ - \text{Cl}^-$, the properties

are evidently connected with the fact that the sodium atom readily loses an electron but can not, apparently, take one from another atom. This may be because the positive part of the atom is so deep in its structure that it exerts little attraction for the electron and little, also, for the negative oxygen. The ease with which metals give up electrons seems to be closely connected with their properties as electrical conductors, though I am not aware that this connection has been pointed out before. It may also be connected with the character of the spectra of metals, the electron of the sodium atom being possibly in orbital motion around it, as Lorenz and others have supposed.

In hydrochloric acid the electron gained by the chlorine atom may perhaps penetrate the atom so deeply as to exert but little attraction for the hydrogen. But it is to be remembered also that while the chlorine atom may take up one electron it may give up seven electrons to other atoms, especially to oxygen.

The speculative character of the suggestions here given, is, of course, clearly recognized. It seems possible, however, that we may sometime know the structure of atoms as we now know the structure of molecules, and it is, perhaps, worth while to indicate some of the lines along which it may be possible to attach problems of this sort. W. A. NOYES.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]
**A CRITICAL SURVEY OF SOME RECENT APPLICATIONS OF THE
ELECTRON CONCEPTION OF VALENCE.**

BY HARRY SHIPLEY FRY.

Received January 2, 1912.

The purpose of this paper is to present some applications of the electron conception of valence and to discuss their bearing upon the assumptions postulated by K. George Falk¹ in his article on the electronic structure and ionization constants of the organic acids.

Falk states that the organic acids may be divided into four classes in which the ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of the α -carbon atom. The principles upon which the direction of valences are assumed to depend are based upon the corpuscular-atomic hypothesis of Sir J. J. Thompson according to which the linkages or bonds between the atoms in a molecule are formed by the transfer of corpuscles or electrons.

Under the sub-title of "Theoretical Considerations" Falk records the following statements:

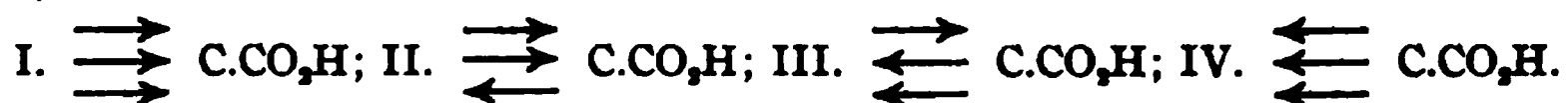
(A) "The principles upon which the directions of valence are assumed to depend were explained in the first paper. (THIS JOURNAL, 32, 1637-54.) It may suffice to

¹ THIS JOURNAL, 33, 1140 (1911). "The Electron Conception of Valence." II. "The Organic Acids."

state here that for a single bond the corpuscle for the carbon-hydrogen union is assumed to pass from the hydrogen to the carbon, the former becoming positively charged, the latter negatively, while for the carbon-chlorine union, the corpuscle passes from the carbon to the chlorine."

(B) "The arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond."

(C) "A classification of the acids will be given here which depends upon the direction of the valences by which the α -carbon atom is combined with the other atoms in the molecule. This divides the acids into four classes which may be formulated as follows:



"The acids belonging to class I are those in which three electropositive groups are combined with the α -carbon atom; those belonging to class II, two electropositive and one electronegative; to class III, one electropositive and two electronegative. The ionization constants are found to increase in the order of the classes I, II, III, IV. The acids represented by formula IV, such as trichloroacetic acid, are too highly ionized to give satisfactory dissociation constants, and will not be considered here."

Statements (A) and (B) constitute the principles by which Falk determines the direction of a bond in the structural formulas of the compounds under consideration. An arrow ($\text{H} \longrightarrow \text{Cl}$) serves as the symbol both for the bond of union and for the direction of the transfer of the corpuscle (electron or negative charge), from one atom to another. Accordingly, one end of a bond corresponds to a positive, while the other end corresponds to a negative charge. Therefore, it is preferable in the following discussion to indicate the polarity of each end of a bond by employing formulas of the type, $\text{H}^+ \text{---} \text{Cl}^-$.

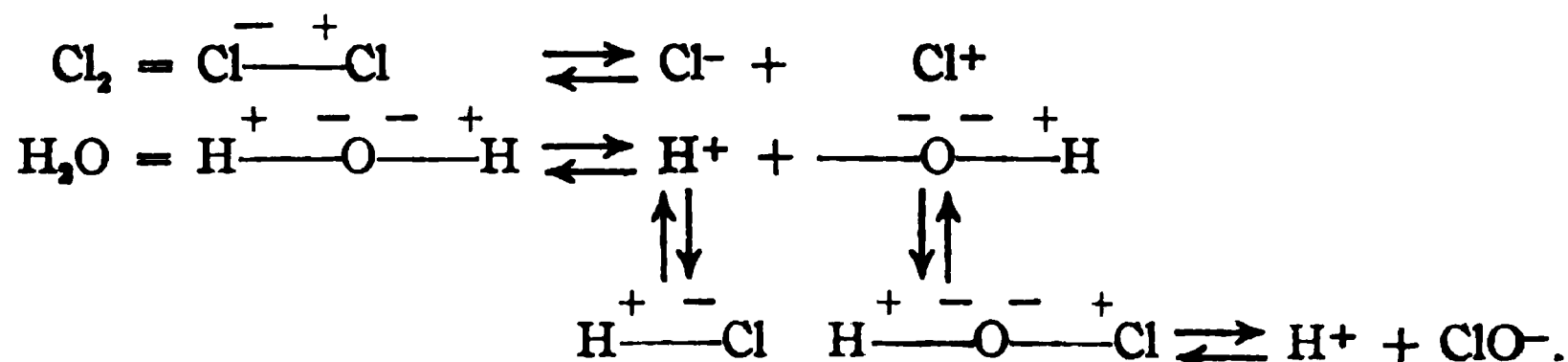
Falk assumes (in statement A) that for a single bond the corpuscle for the carbon-hydrogen union passes from the hydrogen to the carbon, while for the carbon-chlorine union the corpuscle passes from the carbon to the chlorine. In other words, the hydrogen atom functions positively while the chlorine atom functions negatively in the formulas of the organic acids which he discusses. In his first paper¹ Falk has shown that from the standpoint of the electronic conception of valence, a given atom such as chlorine may function *either positively or negatively*, for Sir J. J. Thompson states² that atoms of one and the same kind may become either positively or negatively electrified by the loss or gain of corpuscles respectively, "and those with charges of opposite sign would combine to form a diatomic molecule." Accordingly molecular hydrogen (H_2) and molecular chlorine (Cl_2) may be represented by the electronic formulas, $\text{H}^+ \text{---} \text{H}^-$ and $\text{Cl}^+ \text{---} \text{Cl}^-$, respectively. These formulas were sug-

¹ THIS JOURNAL, 32, 1637-54.

² "Electricity, and Matter." (Scribner's, 1907), p. 139.

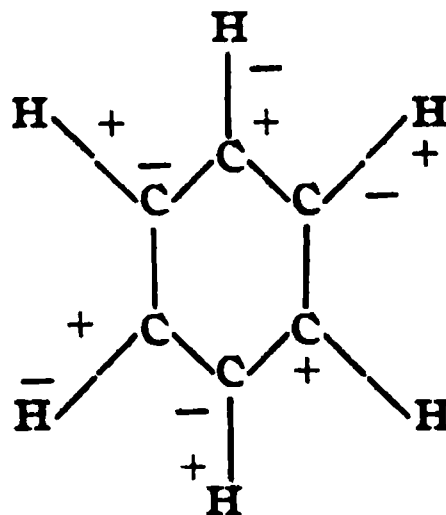
gested at an earlier date by W. A. Noyes,¹ in the following statement: "If we suppose, what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of molecules, it would follow that elementary molecules as well may ionize into positive and negative parts." In the present paper experimental data will be presented, the object of which is to show that in some carbon-chlorine unions the corpuscle passes from the chlorine to the carbon. In other words, the chlorine atom may function positively. A hydrogen atom may also function negatively.

Molecular chlorine, as indicated above, possesses the formula $\text{Cl}^{\ominus}-\text{Cl}^{\oplus}$. Water, electrolytically dissociated, yields positive hydrogen ions; hence the electronic formula, $\text{H}^{\oplus}-\text{O}^{\ominus}-\text{H}^{\oplus}$. The interaction of chlorine and water according to the equation, $\text{Cl}_2 + \text{HOH} \rightleftharpoons \text{HCl} + \text{HOCl}$, must be represented electronically as follows:



Therefore in the oxygen-chlorine union the corpuscle passes from the chlorine atom to the oxygen atom, or in other words the chlorine atom in hypochlorous acid functions positively. Is there any evidence that chlorine may function positively when in combination with carbon?

In an earlier paper² I extended the electronic conception of positive and negative valences to the atoms constituting the benzene molecule. In every possible symmetrically constituted electronic formula for benzene it was shown that the hydrogen atoms in positions, 1, 3, and 5 function negatively while those in positions 2, 4, and 6 function positively. Omitting centric linkages and double bonds, the abbreviated electronic formula of benzene is represented in the following figure:



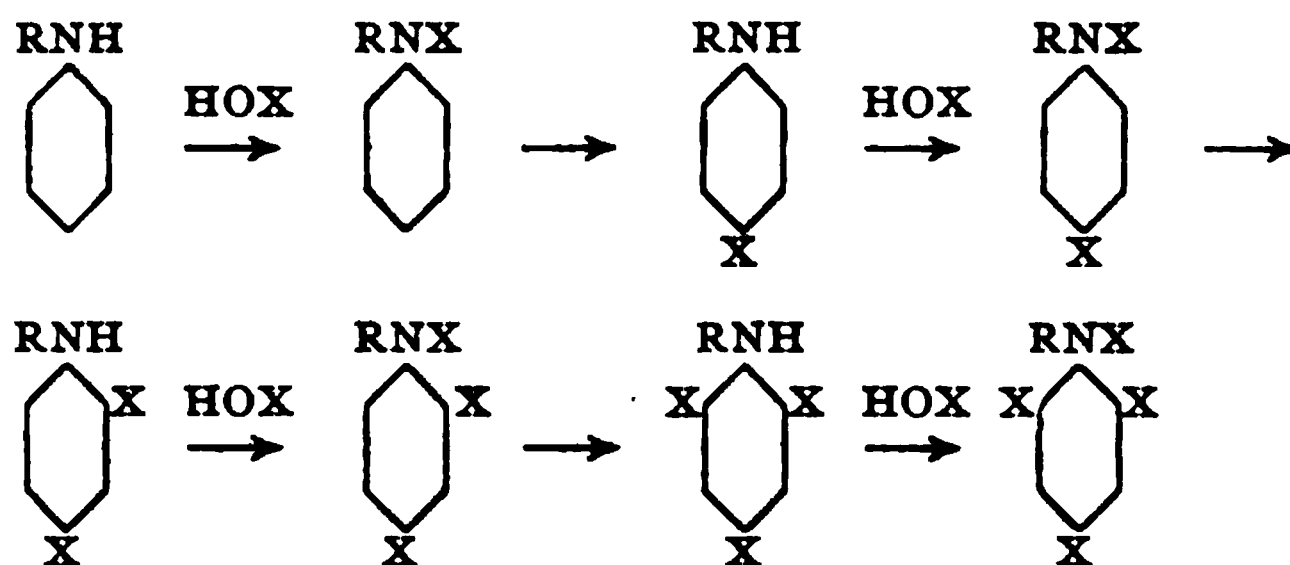
¹ THIS JOURNAL, 23, 460 (1901).

² Fry, *Z. physik. Chem.*, 76, 385 (1911); THIS JOURNAL, *Proceed.*, 30, 34 (1908).

This formula presents a structural basis for the similarity in behavior of the ortho and para positions in contra-distinction to the meta positions. If a given hydrogen atom or substituent is negative, then the hydrogen atoms or substituents ortho and para to it are positive while those meta to it are each negative; and *vice versa*. This formula rendered possible an explanation of the Crum Brown and Gibson Rule¹ for the formation of disubstitution derivatives of benzene and various rearrangement reactions.

Let it now be observed in the electronic formula of benzene that in the carbon-hydrogen unions of positions 1, 3, and 5, the corpuscle passes from the carbon to the hydrogen; in positions 2, 4, and 6, the corpuscle passes from the hydrogen to the carbon. Accordingly, chlorine atoms occupying positions 2, 4, and 6 must function positively. Some of the experimental facts, which show that chlorine atoms in positions 2, 4, and 6 are positive, are as follows:

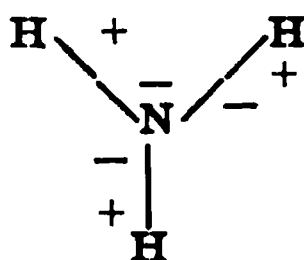
Chattaway and Orton,² in a study of the characteristic rearrangements of the substituted nitrogen halides, show that acetanilide, on treatment with hypochlorous acid, yields phenyl acetyl nitrogen chloride, which is readily transformed into *p*-chloroacetanilide. Treatment of this latter compound with hypochlorous acid gives *p*-chlorophenyl acetyl nitrogen chloride, which is transformed into 2,4-dichloroacetanilide. Proceeding thus the final product is 2,4,6-trichlorophenyl acetyl nitrogen chloride, which will not undergo rearrangement. These successive changes are represented in the following formulas: (R = formyl, acetyl, or benzoyl; X = Cl, or Br):



Why does the halogen atom which wanders from the nitrogen invariably assume a position in the nucleus para or ortho to the amino group, provided these positions are unoccupied? Aniline is a derivative of ammonia. Each hydrogen atom of ammonia is equivalent and functions positively; hence the electronic formula,

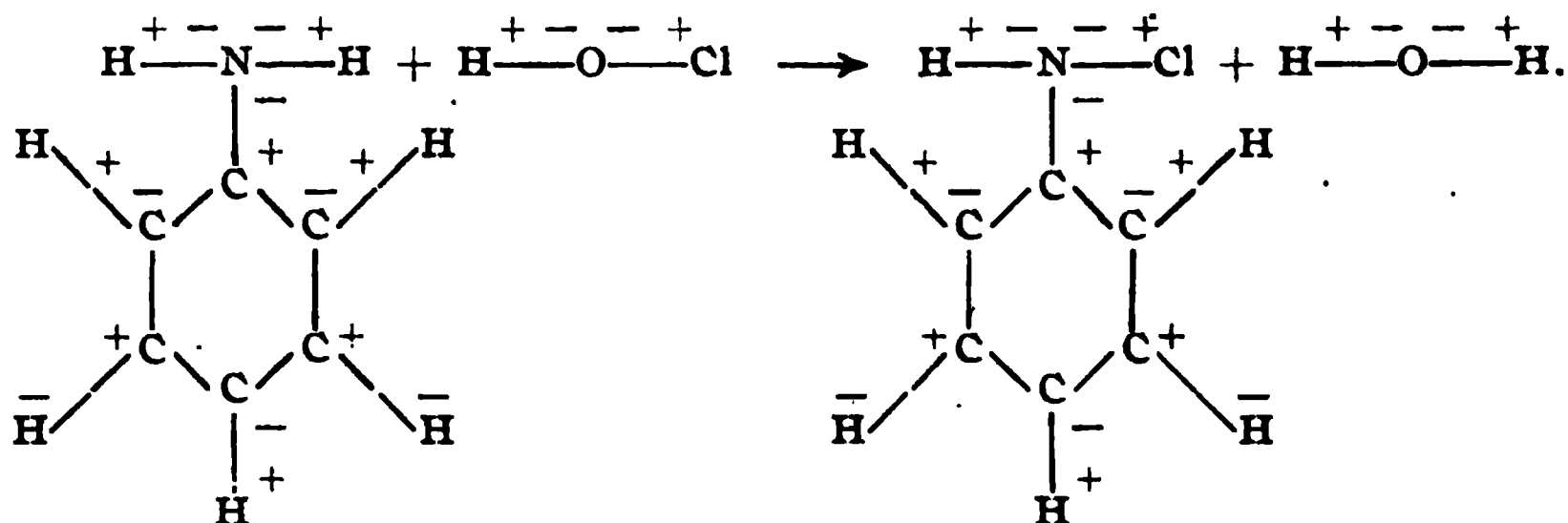
¹ *J. Chem. Soc.*, 61, 366 (1892).

² *Ibid.*, 75, 1046. *Ber.*, 32, 3572.



The radicle —NH_2 is therefore negative and accordingly must occupy the position of a negative hydrogen atom of the benzene nucleus. The electronic formula of aniline and its interaction with hypochlorous acid

($\text{H} \text{---} \text{O} \text{---} \text{Cl}$) are indicated in the following equation:

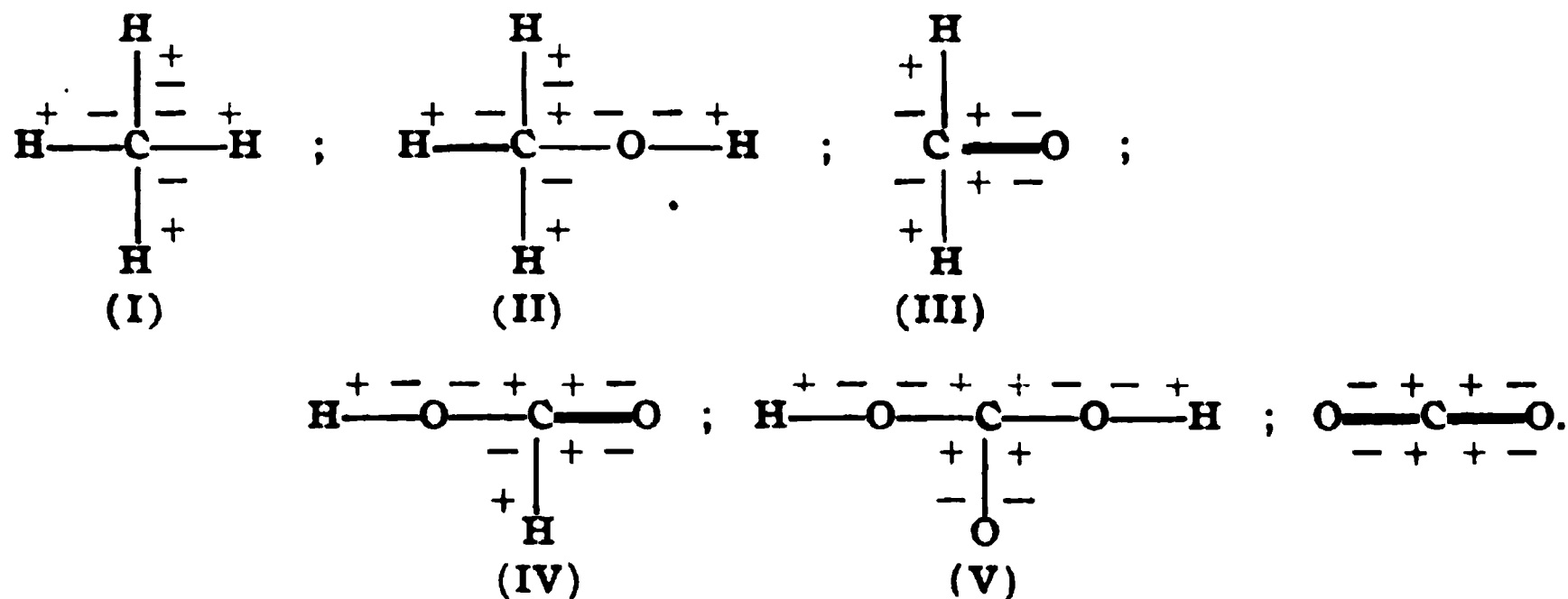


Therefore in the process of transformation of phenyl acyl nitrogen halide into its less labile isomeride, it is self-evident that the halogen atom which functions positively can only exchange positions with a positive hydrogen atom of the nucleus; that is, in passing from the nitrogen to the nucleus it must enter either the para or ortho positions with respect to the attachment of the $\text{NH}_2\text{—}$, or RNH— radicle, which functions negatively. When the para and both ortho positions are occupied, as in 2,4,6-trichloroacyl nitrogen chloride, rearrangement is both actually and theoretically impossible. This constitutes a proof of the identity of polarity of the positions 2, 4, and 6, of the benzene nucleus, each of which is occupied by a positive chlorine atom in the compounds noted above.

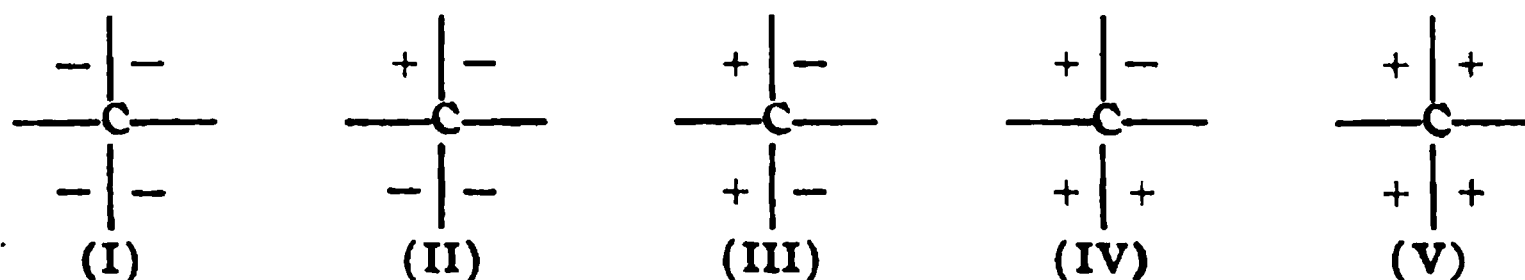
Further evidence for the existence of halogen atoms, which function positively as well as negatively, is given in a previous paper.¹ In this connection Falk's second assumption (statement B), that "the arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond," is subject to discussion. According to the corpuscular-atomic hypothesis a given atom may function either positively or negatively. This is actually the case with chlorine in the compounds previously discussed. How then, for instance, does the position of chlorine in the periodic system determine whether it is to function positively or negatively? Furthermore, it has been demonstrated that if the valence of an element is (n), it may function, from the standpoint of the electron

¹ Fry, *Z. physik. Chem.*, 76, 393 (1911).

conception of valence, in $(n + 1)$ different ways. For example, consider the valences of the carbon atom¹ in the electronic formulas of methane, methyl alcohol, formaldehyde, formic and carbonic acids. If in these compounds the hydrogen atoms function positively and the oxygen negatively, then the following electronic formulas result:

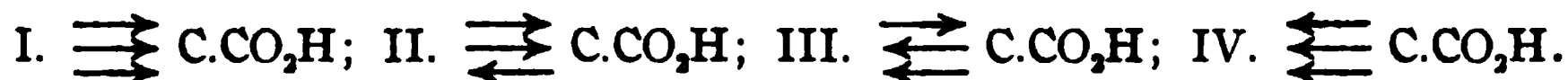


The valence (n) of carbon is 4; the number of ways in which the carbon atom may function ($n + 1$) is 5. The five types as derived from the above electronic formulas are respectively as follows:



These types represent the successive stages of oxidation in the transition from methane to carbonic acid, or its anhydride. Hence it follows that the particular types of carbon atoms, or in other words, *the direction of the valences of the carbon atom in its compounds, can not be determined by the position of carbon in the periodic system, but depends solely upon the polarity of the atoms (or radicles) which are combined with the carbon atom.*

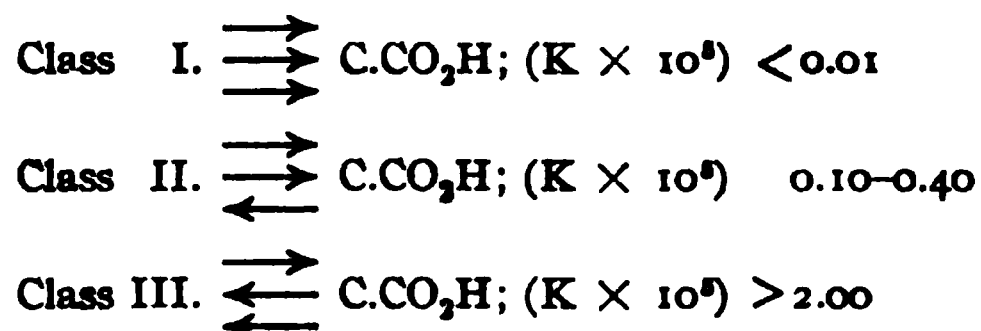
There now remains for consideration statement (C). Falk states that "in considering the structure of the organic acids, it is evident that the α -carbon atom (the one combined directly with the carboxyl group) influences the ionization constant of the acid to the greatest extent." A classification of the acids is then presented "which depends upon the direction of the valences by which this α -carbon atom is combined with the other atoms in the molecule." This divides the acids, according to Falk, "into four general classes which may be formulated as follows:



"The acids represented by formula IV are too highly ionized to give

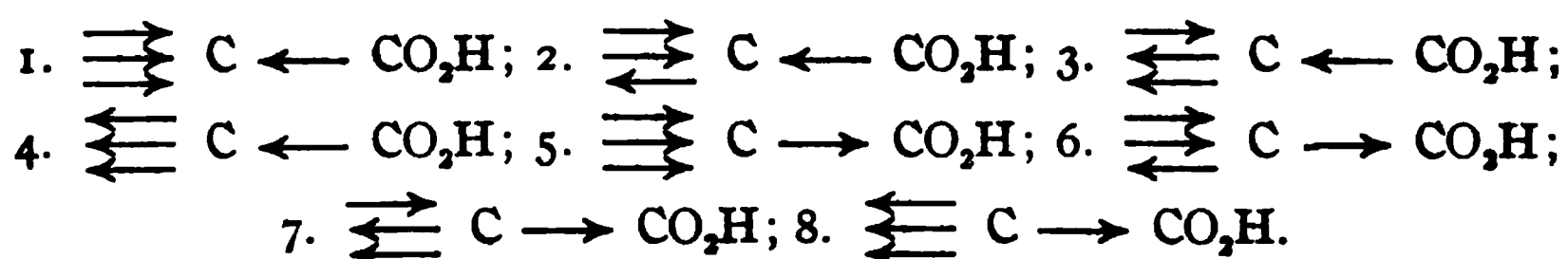
¹ Fry, *Z. physik. Chem.*, 76, 405 (1911).

satisfactory dissociation constants, and will not be considered in detail here." Thus Falk virtually reduces the division of the organic acids into three classes in which the ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of the α -carbon atom. Falk then proceeds to show that "the class to which any given acid belongs may readily be ascertained as the composition taken in connection with the dissociation constant shows the structure of the α -carbon atom." He then assigns for each class of acids the corresponding approximate ionization constants as follows:



Falk then states "that substituents may exert constitutive effects resulting in constants for the acids between the values given for the classes, but a study of the composition should indicate in most cases the class to which an acid may be assigned."

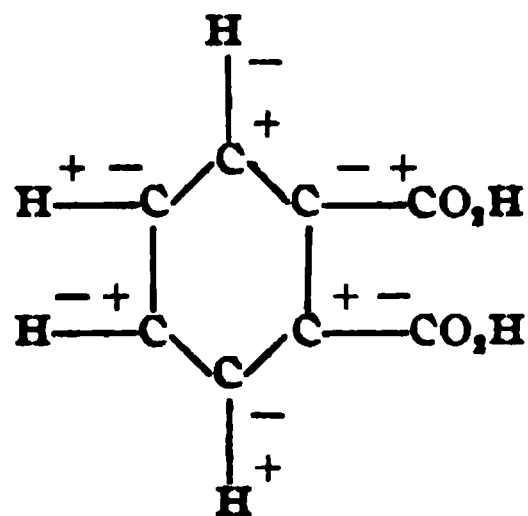
The theoretical objections to Falk's classification must be considered first. Falk has plainly stated that his classification "depends upon the direction of the valences by which the α -carbon atom is combined with the other atoms in the molecule." In direct contradiction to this statement Falk has not considered the direction of the valence or bond between the α -carbon atom and the carbon atom of the carboxyl group. In other words, he considers only three of the four valences of the α -carbon atom, omitting in his discussion the fourth valence, which undoubtedly is the most important since it binds the α -carbon atom to the carboxyl group and thereby determines the polarity of the radicle attached to carboxyl. Therefore, in place of there being only four classes of organic acids, the theory demands eight which must be represented as follows:



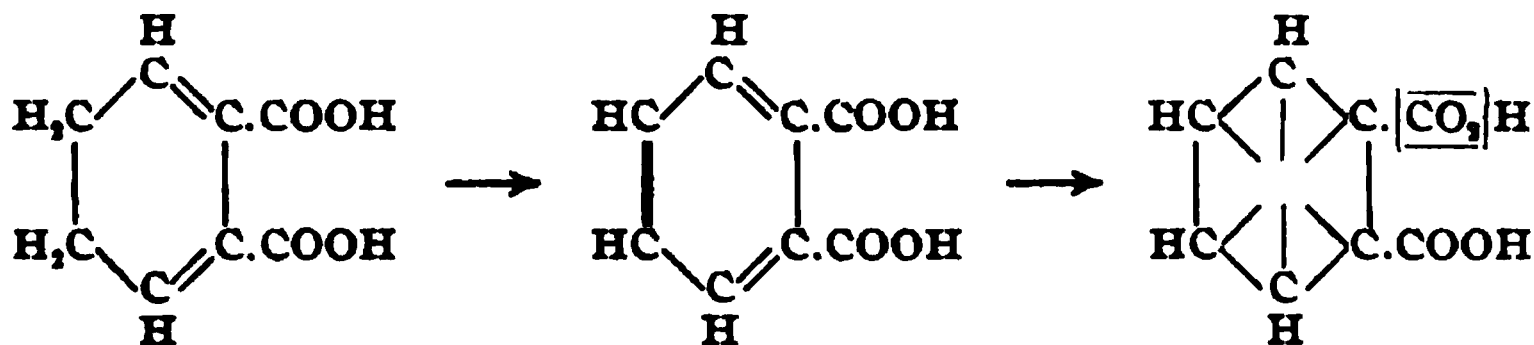
Falk has assigned approximate values of the ionization constants to only three classes of acids. What is to be done with the eight classes which are demanded by this theory?

Experimental facts will now be considered which show that the direction of the valence which binds the α -carbon atom to the carboxyl group has a definite influence upon the property of the compound, or more particularly upon the property of the carboxyl radicle itself. A com-

pound containing two carboxyl groups should be chosen for discussion with the hypothetical requirement that the direction of the valence binding one carboxyl group be opposit to the direction of the valence binding the other. Such a condition would be fulfilled in benzene derivatives containing carboxyl radicles on adjacent carbon atoms of the nucleus. Since hydrogen atoms so attached have been shown to be of opposit polarity, it follows that in phthalic acid one carboxyl radicle functions negatively while the other functions positively, as indicated in the following formula:



Is there any experimental evidence to justify this difference in the attachment of the carboxyl groups to the nucleus? Baeyer¹ has shown that the $\Delta^{3,5}$, $\Delta^{2,4}$, and $\Delta^{2,6}$ dihydrophthalic acids yield benzoic acid on oxidation. He attributes this to a shock (Erschütterung) to the α -carbon atom which causes it to lose carbon dioxide, this effect being associated with the change from ethylene to centric linkages, thus:



Bruhl,² in a critical examination of Baeyer's "Erschütterung theory," asks why only one molecule instead of two molecules of carbon dioxide is removed from the acids in question, and has sought to explain the chemical behavior of the dihydro acids on the simple basis of their difference of stability, which view has the advantage of being independent of any structural hypothesis. But Bruhl, according to Cohen,³ "fails to perceive that by avoiding any reference to structure as affecting stability, is begging the question." It must then be concluded that up to the present time there is no satisfactory structural explanation as to why only one molecule of carbon dioxide instead of two is removed from the several dihydrophthalic acids investigated by Baeyer.

¹ *Ann.*, 269, 178 (1892).

² *J. prakt. Chem.*, [2] 49, 229 (1894).

³ "Organic Chemistry" (Longmans, Green and Co.), 1907, p. 461.

one molecule instead of two molecules of carbon dioxide is removed from the several phthalic acids noted above, and, furthermore, is evidence that the direction of the valence which binds a carboxyl radicle to a compound has a definit influence upon the properties of the radicle and the compound, and, therefore, is not to be disregarded in any applications of the electron conception of directive valences.

Summary.

(1) From the standpoint of the electronic conception of positive and negative valences, an atom, such as chlorine or a univalent radicle, may function either positively or negatively. Before such atom, or radicle, is assumed to be either positive or negative in any particular compound the polarity should be determined experimentally. In this connection the halogen atoms in 2,4,6-trichlorophenyl acetyl nitrogen halides and other compounds, have been shown to function positively. From the position of the halogen atoms in the periodic system they would ordinarily be assumed to function negatively.

(2) The statement that the arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond is subject to extension since it has been shown that an element whose valence is (n) may function in ($n + 1$) different ways. For instance, the tetravalent carbon atom is shown to function according to five different types depending upon its valences being all positive, all negative, or some positive and others negative. These five types are also shown to correspond to successive stages of oxidation illustrated in the compounds, methane, methyl alcohol, formaldehyde, formic acid, and carbonic acid and carbon dioxide.

(3) Falk's classification of the organic acids which he states "depends upon the direction of the valences by which the α -carbon atom is combined to the other atoms in the molecule," is incomplete since he fails to take into account the direction of the valence which binds the α -carbon atom to the carboxyl group. When this valence is considered, the theory demands eight classes of organic acids: Falk postulates only four classes, and considers experimental data for only three classes.

(4) The direction of the valence which binds the α -carbon atom to the carboxyl group is of prime importance since it determines the polarity of the radicle attached to carboxyl and has a definit influence upon the behavior of the carboxyl group itself. This is evinced by the explanation given for the fact that only one instead of two molecules of carbon dioxide is removed from certain phthalic acids in the transformations described by Baeyer.

Further applications of the electronic conception of positive and negative valences are reserved for subsequent papers.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

3-ETHYLHEXANE.

BY LATHAM CLARKE AND EMILE RAYMOND RIEGEL.

Received March 4, 1912.

3-Ethylhexane, $\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$, has been synthesized and studied as a part of the researches of one of us on the paraffin hydrocarbons.¹ It is a liquid with a faint odor, boils at $118.8\text{--}119.0^\circ$, under 766 mm., has, at 15° , the specific gravity 0.7175, compared to water at 15° , and shows an index of refraction, $N_D(25^\circ) = 1.3993$.

Next to the normal, this octane probably has the highest boiling point of any, this statement being founded on the following reasoning: The boiling point of 2-methylheptane is 116° , of 3-methylheptane 117.6° , of 4-methylheptane 118° , so that in moving a methyl group from the end of the chain towards the center, a steady rise of boiling point is observed.

It is now true that an ethylhexane will have a higher boiling point than a methylheptane, for 2-methylheptane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, boils at 116° , while 2-ethylhexane (regarding 3-methylheptane for the moment as 2-ethylhexane), $\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{—CH}_2\text{CH}_3$, boils at 117.6° . Just as the boiling point of 3-methylheptane is higher than that of 2-methylheptane, so the boiling point of 3-ethylhexane should be higher than that of 2-ethylhexane, and, as a matter of fact, 3-ethylhexane boils at $118.8\text{--}119.0^\circ$. Since it is well known that hydrocarbons containing quaternary carbon atoms boil lower than those containing tertiary carbon atoms, all of the former class will have lower boiling points than the methylheptanes. It is apparent, therefore, that, next to normal octane, 3-ethylhexane has the highest boiling point of any octane.

The hydrocarbon isolated by Mabery² from Ohio petroleum and described by him as an octane of the boiling point 119.5° at 760 mm. was probably 3-ethylhexane. (In the same paper Mabery mentions another octane obtained from Ohio petroleum, boiling at $124\text{--}125^\circ$. This can be no other than normal octane.)

3-Ethylhexane contains a normal propyl chain—it may in fact be called diethyl-normal-propylmethane. The corresponding compound containing an isopropylmethane (or 2-methyl-3-ethylpentane), $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$, was prepared in this laboratory in 1908.³ The properties of the two compare as follows:

	Boiling point.	Mm.	Specific gravity $15^\circ/15^\circ$.	Index of refraction $N_D(25^\circ)$.
3-Ethylhexane	118.9°	766	0.7175	1.3993
2-Methyl-3-ethylpentane . . .	114	760	0.7084	1.3996

¹ See Clark, *THIS JOURNAL*, 33, 520 (1911). Clarke and Beggs, *Ibid.*, 34, 54 (1912).

² Mabery and Hudson, *Am. Chem. J.*, 19, 255.

³ Clarke, *Ibid.*, 39, 574.

The boiling points of these two liquids present an interesting relation.

It has been shown¹ in the case of the octanes previously synthesized, that when we have a methylheptane, and we substitute in one end of the chain a methyl group, the depression in boiling point which takes place is equal to the difference in boiling point between normal *heptane* and the corresponding *methylheptane*. To choose a specific example, the boiling point of 2-methylheptane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, is 116.0° . The boiling point of 2,5-dimethylhexane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{---CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$, is 108.25° , but this is 7.75° lower than the boiling point of 2-methylheptane, and is very nearly equal to the difference in boiling point between normal heptane and 2-methylhexane, *viz.*, 8° . Other examples may be cited² to show that when a methylheptane is compared to a dimethylhexane, the boiling point of the latter is as much below the former as the boiling point of the corresponding methylhexane is below that of normal heptane. This rule appears to hold except in cases where the substituting methyl groups are on adjacent carbon atoms, when a boiling point several degrees higher than the "calculated" is observed. Thus the boiling point of 3-methylheptane, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, is 117.6° . We should now calculate the boiling point of 2,3-dimethylhexane, $\text{CH}_3\text{CH}(\text{CH}_3)(\text{CH}_3)\text{CHCH}_2\text{CH}_2\text{CH}_3$, as 109.6° , since we change here from a C₇ straight chain to an "iso" chain, and so we should expect the boiling point of the second compound to be 8° lower than that of the first, or $117.6 - 8 = 109.6^\circ$, but the actual boiling point of 2,3-dimethylhexane is 114° , which is 4.6° higher than the "calculated." In the case of 3,4-dimethylhexane, the actual boiling point is 5.8° higher than the calculated.

Coming back to the case of 3-ethylhexane and 2-methyl-3-ethylpentane, we have in the second compound, on adjacent carbon atoms, a substituting methyl and a substituting ethyl group. By the method already described, we may calculate the boiling point of 2-methyl-3-ethylpentane, and see if this rule of the elevation of a boiling point by substituting methyl groups on adjacent carbon atoms holds also in the case of a methyl and an ethyl group. The boiling point of 3-ethylhexane is 118.9° . The boiling point of 2-methyl-3-ethylpentane should be as much below that of 3-ethylhexane as the boiling point of 2-methylpentane is below that of normal hexane, *viz.*, 6.8° , so that the boiling point of 2-methyl-3-ethylpentane should be 112.1° . The actual boiling point is 114° , or nearly two degrees higher. This shows then that when alkyl groups are substituted on adjacent carbon atoms, the boiling point of the compound will be several degrees higher than in compounds where the substituting alkyl groups are separated by one or more CH_2 groups.

¹ Clarke, *THIS JOURNAL*, 33, 520.

² Clarke, *l. c.*

The boiling points of the xylenes are of interest in this connection. *p*-Xylene boils at 138° , *m*-xylene at 139.2° , while *o*-xylene, in which the methyl groups are on adjacent carbon atoms, boils at 142° .

It is worthy of note that the specific gravity of 3-ethylhexane is nearly the same as that of 3-methylheptane, the figures being 0.7175 and 0.7176, respectively, at 15° , compared to water at 15° . The specific gravity of 3-ethylhexane is greater than that of 2-methyl-3-ethylpentane, viz., 0.7175 and 0.7084, but the indices of refraction ($N_D(25^{\circ})$) are very close, 1.3993 for the first named, and 1.3996 for the second.

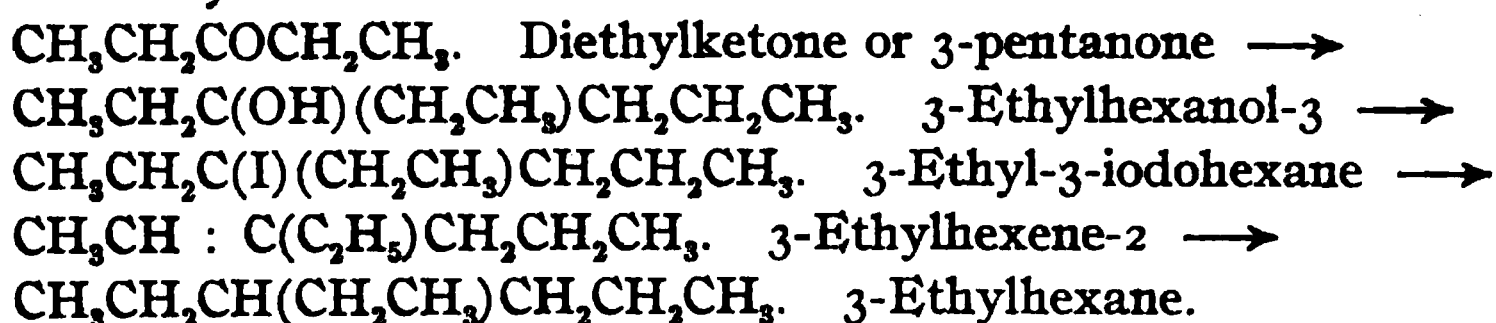
Special Theoretical.

Two methods were considered for the synthesis of 3-ethylhexane.

First Method.—The first consisted in subjecting diethylketone to the Barbier-Grignard reaction, using normal propylmagnesium iodide, by which the alcohol, 3-ethylhexanol-3 was formed. This was converted into the corresponding carbinol iodide and treated with alcoholic potash, which split off hydriodic acid and gave an octylene, 3-ethylhexene-2. By reduction the last was saturated to 3-ethylhexane.

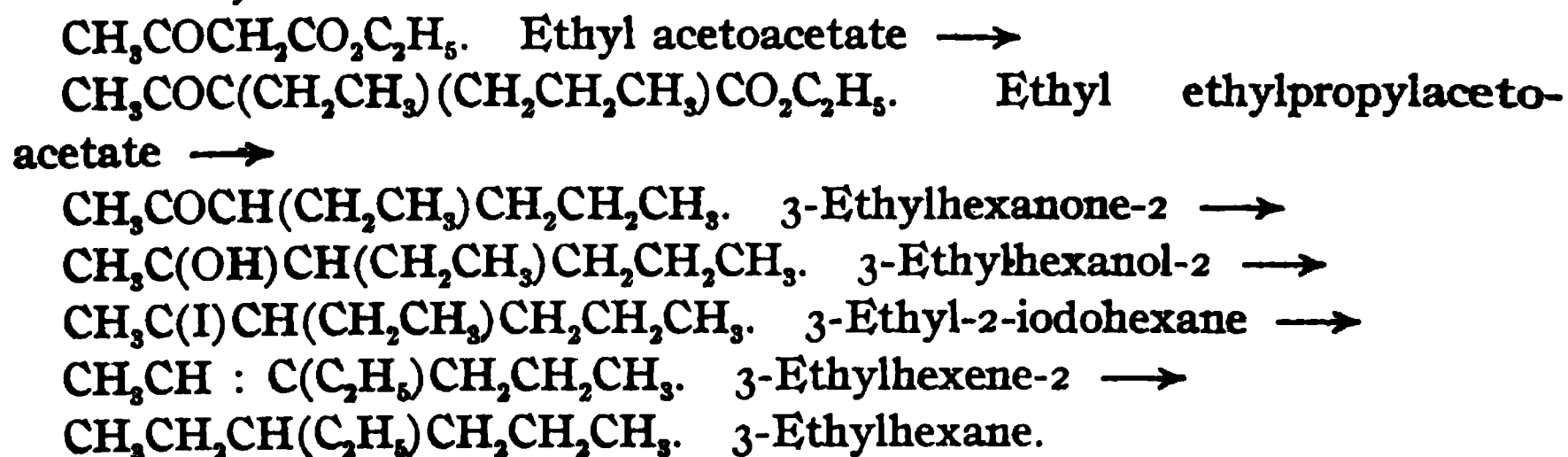
This method was very satisfactory, the yields were very good in all reactions, and the fractionation of each compound was carried on without trouble.

Summary.



Second Method.—This was not carried to a successful conclusion. The plan was as follows: Starting with ethyl acetoacetate, prepare the ethyl normal propyl derivative by replacement of the methylene hydrogen atoms in turn by ethyl and normal propyl groups. This could then be saponified giving the ketone, 3-ethylhexanone-2. By reduction an alcohol would be formed, 3-ethylhexanol-3, and the latter could be converted into the carbinol iodide, treated with alcoholic potash to produce the octylene, 3-ethylhexene-2, and reduced to 3-ethylhexane.

Summary.



This process was abandoned because of the difficulty in obtaining a sufficient quantity of the ketone, 3-ethylhexanone-2, in the proper grade of purity. The introduction of both an ethyl and a normal propyl group into ethyl acetoacetate is possible, but not easy, and gives a variety of products. For example, if the ethyl group be introduced first, a certain amount of the diethyl derivative is also formed, and the propyl group is very slow in substituting on later treatment, this mixture cannot be satisfactorily fractionated, so the whole must be saponified, and the resulting ketones fractionated. It did not seem worth while to prepare the hydrocarbon by this method, which is so laborious as compared to the first mentioned.

Experimental Part.

First Method.—3-Ethylhexanol-3, $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, was made from diethylketone by the action of normal propylmagnesium iodide. The diethylketone was obtained from Kahlbaum and boiled at $101\text{--}103^\circ$. It was fractionated and that boiling at $101.2\text{--}101.8^\circ$ at 756 mm. was used in the subsequent Barbier-Grignard reaction.

Twelve grams of magnesium turnings were dissolved in a mixture of 90 grams of dry normal propyl iodide and 90 grams of anhydrous ether. To the solution 43 grams of diethylketone dissolved in two volumes of dry ether were added, allowed to remain at rest for thirty minutes, when the organo-magnesium compound was decomposed in the usual way with water and dilute hydrochloric acid. During the treatment with water and acid the reaction flask was kept cold by immersion in a tank of ice water. The ethereal layer, containing the desired carbinol, was separated and dried over potassium carbonate, the ether was distilled off and the residue fractionated, yielding 50 grams of 3-ethylhexanol-3, boiling at $155\text{--}159^\circ$ at 756 mm.

This experiment was repeated three times, giving a total yield of 150 grams of the carbinol.

Subst., 0.1969; CO_2 , 0.5316; and H_2O , 0.2430.

Calculated for $\text{C}_8\text{H}_{18}\text{O}$: C, 73.85; H, 13.60

Found: C, 73.63; H, 13.81

Properties.—This carbinol has an odor like that of musty apples. It is miscible with the common organic solvents but not with water.

3-Ethyl-3-iodohexane, $\text{CH}_3\text{CH}_2\text{C}(\text{I})(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, and its *Conversion into 3-ethylhexene-2*, $\text{CH}_3\text{CH} : \text{C}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$.—To 65 grams of 3-ethylhexanol-3, 6.5 grams of red phosphorus were added, and 64 grams of iodine gradually introduced into the mixture. During the addition of the iodine, the reaction flask was kept cool. At the end of one hour, the flask was heated on the steam bath for five hours. The resulting carbinol iodide was washed with water, and filtered to remove

unchanged phosphorus, but was not distilled. It was converted directly into the octylene.

The strong alcoholic potash solution was prepared and the carbinol iodide added to it with shaking. The mixture was heated on the water bath for two hours or so, the flask being fitted with a reflux condenser, after which a downward condenser was attached and the mixture distilled until no more octylene came over. Alcohol and this octylene form a soluble binary mixture of minimum boiling point and all the hydrocarbon passes off during the first part of the distillation. By dilution of the alcoholic distillate with water, the octylene separated as a floating layer, was separated, dried over calcium chloride and distilled. Thirty grams were obtained boiling at $119.6\text{--}120.5^{\circ}$ at 769 mm. This experiment was repeated and gave slightly more than 30 grams of octylene of the above boiling point.

Subst., 0.3157; CO_2 , 0.9868; H_2O , 0.4089.

Calculated for C_8H_{18} : C, 85.71; H, 14.29

Found: C, 85.27; H, 14.37

Properties.—Liquid with a rather strong odor, boiling at $119.6\text{--}120.5^{\circ}$ at 769 mm. It is miscible with the common organic solvents.

3-Ethylhexane, $\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$, was made from the preceding octylene by reduction according to the method of Sabatier and Senderens, by passing the octylene over freshly reduced nickel at a temperature of $160\text{--}180^{\circ}$ in a rapid stream of pure hydrogen.¹ The resulting octane was carefully fractionated, and thirty grams were finally obtained which boiled at $118.8\text{--}119^{\circ}$ under 766 mm. Thirty-five grams of octylene were reduced, and as this was run through the reducing apparatus twice, some was lost through incomplete condensation. Less than a gram of material was rejected in the distillations.

Subst., 0.2935; CO_2 , 0.9012; H_2O , 0.4128.

Calculated for C_8H_{18} : C, 84.21; H, 15.79

Found: C, 83.74; H, 15.74

Properties.—Colorless, very mobil liquid, practically without odor. It boils at $118.8\text{--}119.0^{\circ}$ at 766 mm.; has, at 15° , the specific gravity 0.7175 compared to water at 15° . The index of refraction $N_D(25^{\circ}) = 1.3993$.

Second Method.—Ethyl ethylacetoacetate was made by the method of Conrad,² using sodium ethylate, ethyl acetoacetate and ethyl iodide, and in the usual fashion ethyl ethylacetoacetate was isolated and dried with potassium carbonate. This was treated with sodium ethylate and normal propyl iodide, and the reaction product isolated in the usual way.

¹ See Clarke and Beggs, *THIS JOURNAL*, 34, 59 (1912).

² Conrad and Limpach, *Ann.*, 192, 155.

It was found, however, that the introduction of the propyl group into ethyl ethylacetoacetate was no easy matter and even when the reaction mixture was allowed to stand a week before working up, the yield of ethyl ethylnormalpropylacetoacetate was poor. Somewhat better results were obtained when the propyl group was introduced first, but in no case was the yield satisfactory. The substituted acetoacetate was not purified by distillation but was at once converted into the ketone, or rather a mixture of ketones, since there were several acetoacetic ester derivatives.

Fifty grams of the crude acetoacetate were boiled for ten hours with 75 grams of caustic potash dissolved in 750 cc. of water, the mixture was distilled with steam, the upper layer of the distillate was removed, and dried with calcium chloride. Ten such distillates were then united and carefully fractionated. The products were: 2-pentanone, boiling at 101–104°; 3-ethylpentanone-2, boiling at 136–139°; 2-hexanone, boiling at 126–129°; a small amount of 3-propylhexanone-2, boiling at 173–175°, and (from 500 grams of crude acetoacetate) 25 grams of the desired ketone, 3-ethylhexanone-2, $\text{CH}_3\text{COCH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, boiling at 157.5–158.5° at 761 mm. There was a residue of unketonized acetoacetates.

Properties of 3-Ethylhexanone-2.—Liquid with peppermint-like odor. Boiling point 157.5–158.5° at 761 mm. Miscible with the common organic solvents, but immiscible with water.

3-Ethylhexanol-2, $\text{CH}_3\text{C}(\text{OH})\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$.—Twenty grams of ketone were dissolved in 40 grams of ether and placed in a flask fitted with a long reflux condenser together with 35 grams of water. In small pieces during half an hour, 10 grams of sodium were added. When the sodium had all dissolved, the ether layer was removed, the ether was distilled off, and the residue fractionated, which yielded 19 grams of ethylhexanol-2, boiling at 167.5°–168.5° at 760 mm., and a high-boiling residue of 3 grams, probably a pinacone.

Properties of 3-Ethylhexanol-2.—Liquid with an odor like musty apples, boiling at 167.5–168.5° at 760 mm.; miscible with the common organic solvents; not miscible with water.

On account of the difficulty in preparing a sufficient amount of material, the synthesis of 3-ethylhexane was abandoned at this point, and the study of the hydrocarbon was made with the hydrocarbon prepared by Method I.

Part of the expense of this research was defrayed by a grant from the C. M. Warren Fund for Research, for which we wish to express our gratitude.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

4-METHYLOCTANE.

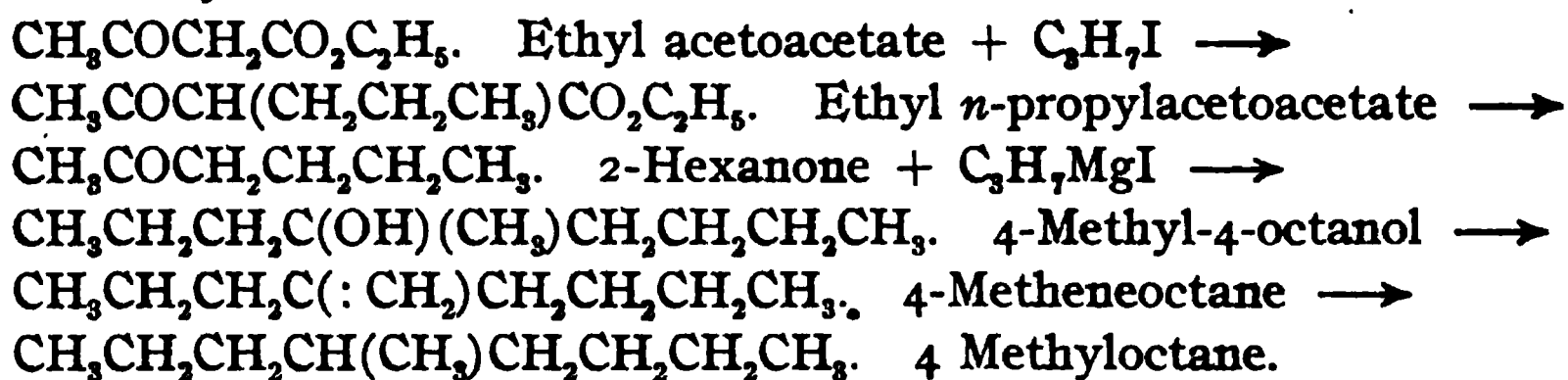
BY LATHAM CLARKE.

Received March 4, 1912.

This hydrocarbon is the third nonane to be synthesized and studied in this laboratory.¹ The syntheses of normal nonane and two others are almost completed and accounts of the work will appear within the next few months.

4-Methyloctane is a liquid, boiling at 141.7–141.9° at 771 mm. It has, at 15°, the specific gravity 0.7320, compared to water at 15°. The index of refraction, $N_D(25^\circ) = 1.4027$.

The method of preparation which seemed the best for 4-methyloctane was the following: Normal propyl iodide was condensed with ethyl sodium acetoacetate, giving ethyl normalpropylacetoacetate, which, on saponification with dilute alkali, yielded the ketone 2-hexanone. This, with normal propylmagnesium iodide, formed the alcohol 4-methyl-4-octanol, containing nine atoms of carbon. By treating the carbinol with iodine and red phosphorus, it was converted into the corresponding carbinol iodide, which last readily lost the elements of hydriodic acid when mixed with alcoholic potash, whereby a nonylene was produced which presumably was 4-metheneoctane, and which on reduction was saturated to 4-methyloctane.

Summary.

In the reaction between normal propylmagnesium iodide and 2-hexanone it was observed that by a slight variation in procedure, either 4-methyloctanol (the expected product) or 4-metheneoctane would be obtained, the latter resulting from a dehydration of the 4-methyloctanol. Ordinarily such reactions as this are carried out by dissolving the required amount of magnesium turnings in a slight excess over the theoretical amount of dry normal propyl iodide mixed with about three volumes of anhydrous ether. To the solution, after thoroughly cooling down in a bath of ice water, the ketone diluted with two volumes of anhydrous ether is added, the mixture allowed to stand a few moments, and the organo-magnesium compound decomposed by treatment with ice water, followed by neutralization with dilute hydrochloric acid. The ether

¹ The first and second were 2,5-dimethylheptane, *THIS JOURNAL*, 34, 54, and 2,4-dimethylheptane, *Ibid.*, 34, 60.

layer is now drawn off, dried with potassium carbonate, the ether distilled off and the residue fractionated. This procedure in the case of normal propylmagnesium iodide and 2-hexanone gave a mixture of the nonylene and alcohol, in the proportion of about one of the former to three of the latter. The fractional separation was difficult. If the temperature was not kept down carefully during the addition of the ketone, the proportion of nonylene would increase, in one case reaching about three parts of the nonylene to one of alcohol. More concentrated solutions in ether as well as excess of acid at the finish were factors which increased the yield of nonylene. Conversely, carefully keeping the temperature in the neighborhood of 0° , and avoiding an excess of acid in the final steps considerably increased the amount of alcohol. In no case was either nonylene or alcohol obtained entirely. In concentrated solutions, the increased production of nonylene is probably due to the heat of reaction, which, being liberated in a smaller sphere, is more intense than in a dilute solution. That this is true is indicated by the fact that when the ketone was added in minute portions with vigorous shaking, thus avoiding any great heat of reaction in one place, the yield of carbinol was much greater.

Experimental Part.

Ethyl Normalpropylacetoacetate, $\text{CH}_3\text{COCH}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{CO}_2\text{C}_2\text{H}_5$.—This was made from sodium ethylate, ethylacetoacetate and normalpropyl iodide by the Conrad and Limpach method.¹ The normalpropyl iodide was prepared from normalpropylalcohol by the action of red phosphorus and iodine and was dried over calcium chloride and redistilled before use. The crude ethyl normalpropylacetoacetate was not distilled but was converted directly into 2-hexanone.

2-Hexanone, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, was made from ethyl normalpropylacetoacetate by boiling for thirty minutes with four molecules of potassium hydroxide in 10% solution. At the end of that time, the ketone was distilled from the alkali with steam, the upper layer of the distillate separated, dried with calcium chloride and fractionated until a fraction was obtained which boiled at $126\text{--}126.5^{\circ}$ at 760 mm. As a rule, the yield of pure 2-hexanone was about 35 grams from 130 grams of ethyl acetoacetate, from 5 to 15 grams were rejected during the fractional distillations. This ketone has already been described.²

4-Metheneoctane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(:\text{CH}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.—As before noted in this paper, the action of normal propylmagnesium iodide and 2-hexanone results in the formation of a mixture of 4-methyloctanol and 4-metheneoctane, the amount of the two, depending on the conditions

¹ *Ann.*, 192, 155.

² Erlenmeyer-Wanklyn, *Ann.*, 135, 144. Schorlemmer, *Ibid.*, 161, 273. Konovalov, *J. Russ. Phys. Chem. Soc.*, 25, 479.

of the experiment. Since 4-metheneoctane was the desired product, the conditions were so regulated as to produce this as far as possible.

The following procedure was usually employed: Twelve grams of magnesium turnings were dissolved in 90 grams of normal propyl iodide, diluted with three volumes of anhydrous ether. Fifty grams of 2-hexanone mixed with one volume of ether were added slowly, the temperature being held between 10° and 15° . The usual treatment with water and acid followed, and after separating and drying with potassium carbonate, the ether solution was fractionated. The separation of the nonylene from the alcohol was accomplished after several fractionations, the former boiling at $142-145^{\circ}$, the latter not very sharply at $178-183^{\circ}$. The yield of nonylene was usually 35-40 grams, of alcohol 20-22 grams. The nonylene was treated with 5% of its weight of iodine, and one-half of 1% of its weight of red phosphorus, and heated an hour or so to convert traces of alcohol into carbinol iodide, filtered to remove phosphorus, washed with water, and distilled with alcoholic potash. The distillate consisted of both nonylene and ethyl alcohol, as these form a soluble binary mixture which distills off on the steam bath. The distillate was treated with water, whereby the hydrocarbon separated as a floating layer which was removed, washed well with water, dried with metallic sodium and fractionated. The major portion boiled at $142-144^{\circ}$ at 768 mm., while much of the fraction boiled at 143.6° . The carbinol mentioned above was mixed with one molecule of iodine and red phosphorus, one-tenth the weight of the iodine used being the weight of the phosphorus taken. The mixture was heated to 70° for three or four hours, filtered through glass wool, and washed with water. The resulting carbinol iodide was refluxed for an hour with alcoholic potash and distilled, the distillate was heated with water, which caused the nonylene to separate as a floating layer which was removed, dried with metallic sodium and distilled. The boiling point of the major fraction was $142-144^{\circ}$ at 768 mm. The total yield of nonylene was usually about 80% of the theoretical or fifty grams, calculated from the fifty grams of hexanone used.

Subst., 0.1852; CO_2 , 0.5807; H_2O , 0.1852.

Calculated for C_9H_{18} : C, 85.71; H, 14.29.

Found: C, 85.52; H, 14.32.

Properties.—Liquid boiling at $142-144^{\circ}$ at 768 mm. It has a faint sweetish odor. It is miscible with the common organic solvents but not with water.

The carbinol was analyzed in the usual way.

Subst., 0.1554; CO_2 , 0.4279; H_2O , 0.1920.

Calculated for $\text{C}_9\text{H}_{20}\text{O}$: C, 75.00; H, 13.88.

Found: C, 75.10; H, 13.83.

Properties.—Colorless, oily liquid with an aromatic sweetish odor. Boiling point, 178–183°. It is miscible with the common organic solvents.

4-Methyloctane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, was prepared from 4-metheneoctane by reduction, the method being that of Sabatier and Senderens, wherein the unsaturated hydrocarbon was passed over freshly reduced nickel at a temperature of 160–180° in a stream of hydrogen. The process was exactly as that described by Clarke and Beggs¹ for the reduction of 2-methyl-5-metheneheptane to 2,5-dimethylheptane.

Twenty-one grams of 4-metheneoctane gave 19 grams of 4-methyloctane, which boiled at 141.7–141.9° at 771 mm. after a fractional distillation in which hardly a gram of hydrocarbon was rejected.

Subst., 0.1720; CO_2 , 0.5334; H_2O , 0.2403.

Calculated for $\text{C}_{10}\text{H}_{20}$: C, 84.37; H, 15.63.

Found: C, 84.57; H, 15.62.

Properties.—Colorless, practically odorless, very mobil liquid. It boils at 141.7–141.9° under 771 mm. Its specific gravity at 15°, compared to water at 15°, is 0.7320 and its index of refraction as determined with the use of a Pulfrich refractometer, $N_D(25^\circ) = 1.4027$.

I am deeply indebted to the C. M. Warren Fund for Research, a grant from which paid the expenses of this work.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY
No. 204.]

RESEARCHES ON QUINAZOLINES (THIRTY-FIRST PAPER). THE ACTION OF METHYL AND ETHYL IODIDES UPON 4-QUINAZOLONES.

BY MARSTON TAYLOR BOBERT AND GEORGE AUGUSTUS GEIGER.²

Received March 1, 1912.

But little information is on record concerning the action of alkyl iodides upon quinazolines.

Paal and Busch³ heated 3-phenyldihydroquinazoline with methyl iodide for 2 hours at 100° and obtained an iodomethylate, another compound (apparently an isomeric iodomethylate), and an iodomethylate periodide.

Knape⁴ heated a methyl alcohol solution of 3-methyl-4-quinazolone with methyl iodide in a sealed tube and obtained the iodomethylate. He also replaced the iodine by hydroxyl through contact with moist silver oxide.

¹ THIS JOURNAL, 34, 59 (1912).

² Read at the Washington meeting of the Society, December 29, 1911.

³ *Ber.*, 22, 2689 (1889).

⁴ *J. prakt. Chem.*, [2] 43, 223 (1890).

Bischler and Barad,¹ by similar treatment of 2-methyl-4-phenyl-quinazoline, obtained an iodomethylate and an iodoethylate.

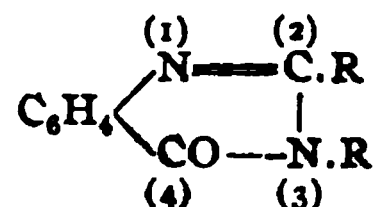
Paal and Neuburger² found that when *m*-aminophenyldihydroquinazoline, in methyl alcohol solution, was heated with excess of methyl iodide in a sealed tube for 12 hours, two molecules of methyl iodide were taken up: one by the quinazoline nucleus, the other methylating the amino group of the *m*-aminophenyl.

Gabriel and Colman,³ working with quinazoline itself, discovered that the iodomethylate could be obtained in the cold or, more rapidly, by heating in a sealed tube, the methyl iodide attaching itself to the nitrogen at position 3. By the action of potassium hydroxide upon this iodomethylate, the corresponding methyl quinazolinium hydroxide was produced.

In the succeeding pages are recorded experiments with methyl and ethyl iodides on various 4-quinazolones, from which the following conclusions are drawn:

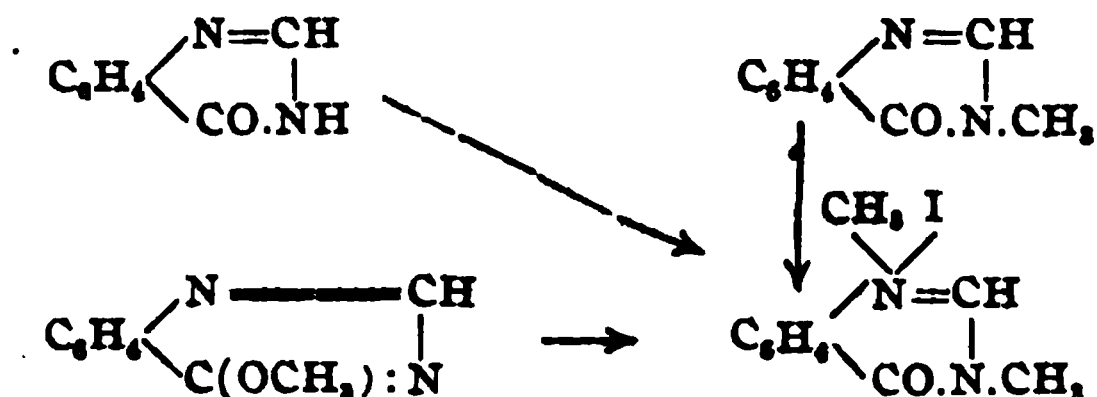
(1) 4-Quinazolones do not add alkyl iodides readily except under pressure and at temperatures of 110° or above.

(2) The iodide adds to the nitrogen in position 1, and not to that in position 3, since the compound obtained by adding methyl iodide to 2-methyl-3-ethyl-4-quinazolone is not the same as that obtained by adding ethyl iodide to 2,3-dimethyl-4-quinazolone. This is what was expected, as the nitrogen in position 1 is the more basic,—that in position 3, due to the adjoining CO group, being more amidic in character:



(3) The iodoethylates are more soluble in water, or in methyl alcohol, than the corresponding iodomethylates, and usually melt lower.

(4) By the action of methyl iodide alone, in excess, 4-quinazolone, 3-methyl-4-quinazolone and 4-methoxyquinazoline, all yield one and the same product, namely the iodomethylate of 3-methyl-4-quinazolone:



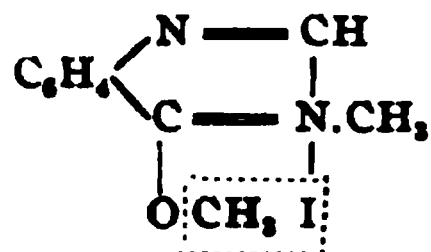
Whether the conversion of the 4-methoxyquinazoline into the iodo-

¹ Ber., 25, 2082 (1892).

² J. prakt. Chem., [2] 48, 563 (1893).

³ Ber., 37, 3651 (1904).

methylate of 3-methyl-4-quinazolone is or is not due to a preliminary addition of methyl iodide to the nitrogen in position 3, with subsequent splitting off again, thus



has not been determined as yet. It is hoped that further work will answer this question.¹ It is worth noting in this connection that, by the action of methyl iodide upon 2-methyl- or 2-styryl-4-quinazolone, the iodomethylates can be obtained without any methylation of the NH group in position 3.

(5) 6-Nitro-4-quinazolones generally refuse to combine with methyl or ethyl iodide.

(6) 2-Styryl-4-quinazolones add methyl iodide more easily than they do ethyl iodide. Styrylquinazolones carrying phenyl, *p*-anisyl, *p*-phenetyl or α -naphthyl radicals in position 3 do not add methyl iodide on 10 hours' heating at 150°. A *p*-tolyl radical in the same position does not seem to interfere.

(7) Generally these alkyl iodide addition products melt at high temperatures and soon thereafter evolve what in the cases tested proved to be the alkyl iodide. Occasionally, they remain in quiet fusion without any such effervescence.

(8) In some cases, the iodine can be replaced by the NO₂ group, by digesting the iodomethylate with silver nitrate.

The following new iodoalkylates of 4-quinazolones are described: iodomethylates of 2-methyl, 2,3-dimethyl, 3-ethyl, 2-methyl-3-ethyl, 3-benzyl, 2-methyl-3-phenyl, 2-methyl-3-*p*-tolyl, 2-methyl-3-*p*-anisyl, 2-methyl-3-*p*-phenetyl, 2-methyl-3- α -naphthyl, 2-methyl-3- β -naphthyl, 2-methyl-3-amino, 2-styryl, 2-styryl-3-methyl, 2-styryl-3-ethyl, 2-styryl-3-*p*-tolyl, 6-nitro-3-methyl, 2-phenylbutadienyl, 2-*m*-methoxy-*p*-hydroxy-styryl; and iodoethylates of 3-methyl, 2,3-dimethyl, 3-ethyl, 2-methyl-3-ethyl, 2-methyl-3-phenyl and 2-styryl.

These iodoalkylates were analyzed by dissolving 0.2–0.3 gram of substance in water, adding a solution of silver nitrate acidified with nitric acid, and warming until the precipitated silver iodide settled. The precipitate was filtered through a Gooch crucible, washed carefully, dried at 110–20° and weighed. When the original substance was insoluble in water even on heating, sufficient alcohol was added to effect solution.

¹ Compare Bogert and Seil, *THIS JOURNAL*, 29, 517 (1907). Bogert and May, *Ibid.*, 31, 507 (1909). May, Dissert., Columbia Univ., 1908.

The preparation of the quinazolones used in the experiments will be found chiefly in previous papers from this laboratory.¹

It is hoped to continue this line of study.

Experimental.

4-Quinazolone and Methyl Iodide.—4-Quinazolone was boiled with methyl iodide, alone or in methyl alcohol solution, but no formation of iodomethylate could be detected. It became necessary, therefore, to carry out the reaction under pressure.

Three grams of the quinazolone and slightly more than an equimolecular amount of methyl iodide were heated together in a sealed tube for 7 hours at 100°. On opening the tube, there was slight pressure evident. The red, crude product was purified by repeated crystallization from methyl alcohol and was thus obtained in small crystals, of faint yellowish tinge, melting at 273–4° (cor.). Yield, 20%. The substance was soluble in water or in alcohol, difficultly soluble or insoluble in ether, chloroform, acetone or benzene.

Another tube was run with two molecules of methyl iodide to one of the quinazolone. The tube contents at the close of the heating possessed a peculiar penetrating odor. The purified product was colorless, melted at 273° (cor.), and was identical with that secured in the first experiment. Yield, 50%.

Calculated for $C_{10}H_{11}ON_2I$: N, 9.27; I, 42.04.

Found: N, 9.28; I, 41.99.

The product is thus an iodomethylate of a methylquinazolone, and is identical with the iodomethylate obtained from 3-methyl-4-quinazolone or from 4-methoxyquinazoline, as a mixture of any two, or of all three, showed the same melting point, and the crystals appeared the same under the microscope.

4-Methoxyquinazoline and Methyl Iodide.—That these substances react to form an iodomethylate has been shown by May.² He gives the melting point of the product as 265° (cor.), and his analysis corresponds to that of an iodomethylate of a methylquinazolone. We have repeated the work and find that the product is the iodomethylate of 3-methyl-4-quinazolone and that when carefully purified it melts at 274° (cor.).

This reaction goes on slowly when cold, and the product is conveniently purified by crystallization from methyl alcohol.

4-Methoxyquinazoline and Ethyl Iodide.—Two grams of the quinazoline were heated with the calculated amount of ethyl iodide for several hours at 100°, and the crude product crystallized from methyl alcohol. Fine

¹ Bogert, Beal and Amend, *THIS JOURNAL*, 32, 1654 (1910). Bogert and Beal, *Ibid.*, 34, 516 (1912). Bogert and Geiger, *Ibid.*, 34, 524 (1912).

² *Loc. cit.*

colorless needles were thus obtained, melting at 249° (uncor.), insoluble in cold water. Yield, 1 gram.

Found: I, 40.90, 40.90; N, 9.42.

These figures do not check with those calculated for the compound expected, and the substance has not yet been identified.

2-Methyl-4-quinazolone and Methyl Iodide.—The quinazolone was boiled for 7 hours with excess of methyl iodide, but no change occurred. A solution of the quinazolone and methyl iodide in methyl alcohol was then boiled for 4 hours with the same result.

When the quinazolone and methyl iodide were heated together at 150° in a sealed tube, the result was a reddish crystallin cake. This cake was dissolved in cold methyl alcohol (in which it is very easily soluble), a few drops of ether added (not sufficient to cause precipitation), and the mixture cooled to -10° . Well-formed crystals separated, and additional crops were secured by treating the mother liquors similarly. The crude substance melts at 220° (uncor.). Yield, poor.

Calculated for $C_{10}H_{11}ON_2I$: N, 9.27; I, 42.04.

Found: N, 9.47; I, 42.05.

A similar product was obtained when two molecules of methyl iodide were used to one of the quinazolone.

In another experiment, at 100° , the product separated as a pale yellow amorphous solid, but its melting point (220°) and analysis showed it to be the same as the above:

Found: N, 9.20; I, 42.18.

The pure compound forms grayish prisms, soluble in water, methyl or ethyl alcohols; difficultly soluble or insoluble in ether, chloroform, benzene or acetone.

3-Methyl-4-quinazolone and Methyl Iodide.—Knape¹ prepared this iodomethylate by heating a methyl alcohol solution of the quinazolone and methyl iodide in a sealed tube for an hour at 100° . If the methyl alcohol be omitted in the preparation, the yield is then nearly theoretical.

The product crystallizes from methyl alcohol in colorless prisms, melting at 274° (cor.). Knape gives no melting point for his product, while May, who also prepared it, gives it as 263° .

Calculated for $C_{10}H_{11}ON_2I$: N, 9.27; I, 42.04.

Found: N, 9.44; I, 42.19.

3-Methyl-4-quinazolone and Ethyl Iodide.—An equimolecular mixture of the two was heated in a sealed tube for 2 hours at 110° . The crude product was recrystallized from methyl alcohol, giving clusters of pale yellowish prisms, melting with effervescence at 230° (cor.). Yield, 40%. The compound is much more soluble in hot water than the isomeric 3-ethyl-4-quinazolone iodomethylate.

¹ Loc. cit.

Calculated for $C_{11}H_{13}ON_2I$: N, 8.86; I, 40.17.

Found: N, 9.14; I, 40.13.

2,3-Dimethyl-4-quinazolone and Methyl Iodide.—This quinazolone when boiled with methyl iodide failed to yield any iodomethylate, so 3 grams of it were heated with the calculated amount of methyl iodide in a sealed tube for 7 hours at 100° . The product crystallized from methyl alcohol in fine colorless crystals which, after three recrystallizations, melted at 245° (cor.). Yield, 90%.

Calculated for $C_{11}H_{13}ON_2I$: N, 8.86; I, 40.17.

Found: N, 9.01; I, 40.40.

It is soluble in water or benzene, very slightly soluble (yellow solution) in acetone, apparently insoluble in ether.

2,3-Dimethyl-4-quinazolone and Ethyl Iodide.—The two were heated together under exactly the same conditions as for the 2-methyl-3-ethyl-4-quinazolone and methyl iodide described beyond. At the close of the heating, the tube contained a mass of fine reddish crystals. Recrystallized from methyl alcohol, colorless glassy needles resulted, melting at 242° (cor.).

Calculated for $C_{13}H_{15}ON_2I$: N, 8.48; I, 38.46.

Found: N, 8.84; I, 38.49.

3-Ethyl-4-quinazolone and Methyl Iodide.—Three grams of the quinazolone were heated with excess of methyl iodide for 2 hours at 110° . The product crystallized from methyl alcohol in thin colorless scales of satiny luster, melting with effervescence at 258° (uncor.); soluble in water or alcohol; difficultly soluble or insoluble in cold water, in acetone, chloroform, ether or benzene. Yield, 3.1 grams.

Calculated for $C_{11}H_{13}ON_2I$: N, 8.86; I, 40.17.

Found: N, 9.13; I, 40.10.

3-Ethyl-4-quinazolone and Ethyl Iodide.—The two were heated together for 2 hours at 110° and the crude product purified by careful crystallization from a mixture of methyl alcohol and ether. The pure substance forms fine, short, pale yellowish needles, melting at 181° (cor.); soluble in water, methyl or ethyl alcohol, acetone, chloroform or benzene; practically insoluble in ether. Yield, 4.5 grams from 2.75 grams of the quinazolone.

Calculated for $C_{13}H_{15}ON_2I$: I, 38.46.

Found: I, 38.51.

2-Methyl-3-ethyl-4-quinazolone and Methyl Iodide.—Two grams of the quinazolone and slightly more than the calculated amount of methyl iodide were heated together in a sealed tube for 4 hours at 110° . The tube then contained a crystallin yellow mass and slight pressure was evident on opening it. The solid material was crystallized from methyl alcohol, in which it is more soluble than the iodomethylate of 2,3-di-

methyl-4-quinazolone. As thus recrystallized, it forms rosets of small, colorless crystals, which melt with effervescence at 220° (cor.).

Calculated for $C_{12}H_{10}ON_2I$: N, 8.48; I, 38.46.

Found: N, 8.63; I, 38.24.

2-Methyl-3-ethyl-4-quinazolone and Ethyl Iodide.—An equimolecular mixture of the two was heated for 2 hours at 110° . The tube then contained a deep red liquid in which were a few crystals. On concentration, this liquid gave a viscous mass, readily dissolving in methyl alcohol or in acetone, but giving no good crystals on cooling. By careful addition of ether to the methyl alcohol solution, a pale yellow pulverulent solid precipitated, melting sharply at 177° (cor.), which appears to be the iodoethylate sought. Yield, very poor. The compound is readily soluble in water.

Calculated for $C_{13}H_{17}ON_2I$: I, 36.90.

Found: I, 37.11.

3-Benzyl-4-quinazolone and Methyl Iodide.—Three grams of the quinazolone and the calculated amount of methyl iodide were heated together for an hour at 110° , and the crude product purified by crystallization from alcohol. Yield, 3.3 grams. The pure substance forms minute, cream colored crystals, melting at 188° (cor.); soluble in water or chloroform; difficultly soluble in acetone; practically insoluble in ether or benzene.

Calculated for $C_{16}H_{14}ON_2I$: I, 33.58.

Found: I, 33.48.

2-Methyl-3-phenyl-4-quinazolone and Methyl Iodide.—A mixture of 2 grams of the quinazolone and the calculated amount of methyl iodide was heated in a sealed tube at 110° , and the crude product crystallized from methyl alcohol, from which it separated in short needles, partly united in clusters or rosettes, and melting with effervescence at 243° (cor.). Yield, 90%.

Calculated for $C_{19}H_{14}ON_2I$: N, 7.40; I, 33.58.

Found: N, 7.54; I, 33.50.

2-Methyl-3-phenyl-4-quinazolone and Ethyl Iodide.—An equimolecular mixture of the two was heated in a sealed tube for 2 hours at 110° . The crystallin product was too easily soluble in methyl alcohol, so it was crystallized from acetone, from which it separated in minute, colorless crystals, melting at 244° (cor.). Yield, not very good.

Calculated for $C_{17}H_{17}ON_2I$: I, 32.38.

Found: I, 32.49.

2-Methyl-3-p-tolyl-4-quinazolone and Methyl Iodide.—The quinazolone and methyl iodide were heated together in a sealed tube for 3 hours at 110° , and the product crystallized first from methyl alcohol and then from ethyl alcohol (to remove a small amount of reddish impurity). Yield, 80%. The pure compound forms pale yellowish plates of satiny

luster, melting with effervescence at 234.5° (uncor.); soluble in water, methyl or ethyl alcohol.

Calculated for $C_{17}H_{17}ON_2I$: I, 32.38.

Found: I, 32.17.

2-Methyl-3-p-anisyl-4-quinazolone and Methyl Iodide.—An equimolecular mixture of the two was heated in a sealed tube for 3 hours at 116° , and the product crystallized from methyl alcohol, yielding colorless nacreous scales, melting with effervescence at 231.5° (cor.); soluble in water, methyl or ethyl alcohol; difficultly soluble or insoluble in ether, chloroform, acetone or benzene. Yield, 3 grams from 2.5 grams of the quinazolone.

Calculated for $C_{17}H_{17}O_2N_2I$: I, 31.11.

Found: I, 31.01.

2-Methyl-3-p-phenetyl-4-quinazolone and Methyl Iodide.—A mixture of the quinazolone with excess of methyl iodide was heated for 3 hours at 110° and the product crystallized from methyl alcohol. Small, pale yellowish crystals were obtained, melting with effervescence at 221° (uncor.); soluble in water, methyl or ethyl alcohol; difficultly soluble or insoluble in ether, chloroform, acetone or benzene.

Calculated for $C_{18}H_{18}O_2N_2I$: I, 30.07.

Found: I, 30.05.

2-Methyl-3- α -naphthyl-4-quinazolone and Methyl Iodide.—A mixture of the quinazolone and methyl iodide was heated in a sealed tube for 3 hours at 110° , and the product crystallized from methyl alcohol. Minute, pale yellowish needles resulted, melting with effervescence at 235° (uncor.); soluble in water, methyl or ethyl alcohol; difficultly soluble or insoluble in ether, chloroform, acetone or benzene. Yield, 2 grams from 3 grams of the quinazolone.

Calculated for $C_{20}H_{17}ON_2I$: I, 29.65.

Found: I, 29.73.

2-Methyl-3- β -naphthyl-4-quinazolone and Methyl Iodide were heated together for 3 hours at 120° and the product, on crystallization from methyl alcohol, gave microscopic, pale brown needles, melting with effervescence at 238° (uncor.), and showing approximately the same solubilities as the α -compound. Yield, theoretical.

Calculated for $C_{20}H_{17}ON_2I$: I, 29.65.

Found: I, 29.80.

2-Methyl-3-amino-4-quinazolone and Methyl Iodide.—Attempts to methylate the amino group in this quinazolone either by the action of methyl iodide, or of dimethyl sulfate, in presence of alkali, failed, the quinazolone being recovered unaltered. By the action of methyl iodide alone, however, a moniodomethylate was obtained.

A mixture of the quinazolone and methyl iodide was heated for an hour at 110° . Longer heating caused considerable decomposition. The

crude product crystallized from methyl alcohol in minute, pale brownish prisms, melting with effervescence at 201° (cor.), and showing similar solubilities to the above naphthyl derivatives. Yield, 2 grams from 3 grams of the quinazolone.

Calculated for $C_{16}H_{17}ON_2I$: I, 40.04.

Found: I, 39.93.

2-Styryl-4-quinazolone and Methyl Iodide.—The addition of the methyl iodide was accomplished by 2 hours' heating at 110° . The product crystallized from methyl alcohol in short, feathery, golden yellow needles, which began to melt at 230° and gave a clear liquid fusion at 235° (uncor.), but, unlike the iodomethylates described above, did not show any effervescence. Yield, 2.5 grams from 3 grams quinazolone. The substance is difficultly soluble in hot water, soluble in methyl or ethyl alcohol, very difficultly soluble or insoluble in ether, chloroform, acetone or benzene.

Calculated for $C_{17}H_{18}ON_2I$: I, 32.54.

Found: I, 32.43.

2-Styryl-4-quinazolone Methyl Nitrate, $C_{16}H_{12}ON_2 \cdot CH_3NO_3$.—In the analysis of the preceding compound, the iodine was precipitated as usual with silver nitrate and the silver iodide filtered out. From the filtrate, on cooling, there separated fine, pale yellowish needles, melting with effervescence at 177° (cor.), which proved to be the corresponding methyl nitrate addition product, the iodine having been replaced by the nitric acid residue. Yield, theoretical.

Calculated for $C_{17}H_{18}O_4N_3$: N, 12.92.

Found: N, 12.96.

2-Styryl-4-quinazolone and Ethyl Iodide.—No addition occurred when these substances were heated together for 3 hours at 110° , and it was found necessary to heat 10 hours at 140° to accomplish the desired result. The iodoethylate crystallizes from methyl alcohol in small, feathery, orange yellow needles, which melt at $217-8^{\circ}$ (uncor.) without effervescence. It is difficultly soluble in hot water, much more soluble in methyl alcohol than the corresponding iodomethylate, moderately soluble in acetone or chloroform, and practically insoluble in ether or benzene. Yield, 1.5 grams from 3 grams quinazolone.

Calculated for $C_{18}H_{17}ON_2I$: I, 31.41.

Found: I, 31.45.

2-Styryl-3-methyl-4-quinazolone and Methyl Iodide.—An equimolecular mixture of the two was heated 4 hours at 110° in a sealed tube. The solid product was crystallized from methyl alcohol, and then appeared in bright, lemon yellow scales, melting with effervescence at 214° (cor.); soluble in a large volume of hot water. Yield, 80%.

Calculated for $C_{18}H_{17}ON_2I$: N, 6.93; I, 31.41.

Found: N, 7.19; I, 31.49.

2-Styryl-3-methyl-4-quinazolone heated with excess of ethyl iodide

for 3 hours at 115° , or for 5 hours at $130-40^{\circ}$, yielded no iodoethylate, but remained unchanged.

2-Styryl-3-ethyl-4-quinazolone and Methyl Iodide were heated together for 2 hours at 115° in a sealed tube. The crude product crystallized from methyl alcohol in pale yellow, glistening plates, melting with effervescence at 207.5° (uncor.); difficultly soluble in water, but much more readily soluble in methyl alcohol than the 2-styryl-3-methyl-4-quinazolone iodomethylate. Yield, 30%.

Calculated for $C_{19}H_{19}ON_2I$:	I, 30.36.
Found:	I, 30.46.

2-Styryl-3-p-tolyl-4-quinazolone and Methyl Iodide.—A mixture of the two was heated for 3 hours at 110° without any change occurring, and it was necessary to heat for 10 hours at 140° to effect the addition. The product crystallizes from methyl alcohol in clusters of beautiful golden yellow needles, melting with effervescence at 219.5° (uncor.); difficultly soluble in water; more soluble in methyl alcohol than the iodomethylate of 2-methyl-3-p-tolyl-4-quinazolone; soluble in ethyl alcohol; difficultly soluble or insoluble in ether, chloroform, acetone or benzene.

Calculated for $C_{21}H_{21}ON_2I$:	I, 26.50.
Found:	I, 26.49.

The following 4-quinazolones failed to add methyl iodide when heated with it for 10 hours at 140° : 2-styryl-3-phenyl, 2-styryl-3-p-anisyl, 2-styryl-3-p-phenetyl and 2-styryl-3- α -naphthyl.

6-Nitro-3-methyl-4-quinazolone and Methyl Iodide.—Six grams of the quinazolone were heated with methyl iodide in a sealed tube for 6 hours at 130° . The crude product crystallized from methyl alcohol in clusters of orange needles, melting sharply at 228.5° (cor.). Yield, 5 grams.

Found: N, 15.80, 15.90; I, 23.36, 23.43.

This corresponds to a compound made up of one molecule of the original quinazolone in union with one molecule of its iodomethylate (N, 15.21; I, 23.0). Under the microscope, the crystals appeared homogeneous. When this substance was crystallized from water, there separated first some of the original quinazolone, then the orange needles just described, and finally the iodomethylate sought.

The latter crystallizes in small, yellow needles, melting sharply at the same point as the orange compound (228.5° , cor.).

Calculated for $C_{19}H_{19}O_2N_2I$:	I, 36.58.
Found:	I, 36.19.

The following nitro 4-quinazolones refused to add methyl iodide under the conditions of our experiments: 6-nitro-2-methyl, 6-nitro-2,3-dimethyl and 6-nitro-2-methyl-3-ethyl.

2-Phenylbutadienyl-4-quinazolone and Methyl Iodide were heated together for 3 hours at 120° . The crude product crystallized from methyl

alcohol in minute, salmon crystals, melting with slight effervescence at 232.5° (cor.); insoluble in water, but soluble in dilute ethyl alcohol. Yield, 1 gram from 2 grams quinazolone.

Calculated for $C_{11}H_{11}ON_2I$: I, 30.51.

Found: I, 30.43.

2-m-Methoxy-p-hydroxystyryl-4-quinazolone and *Methyl Iodide* were heated together for 3 hours at 120° . The crude product crystallized from methyl alcohol in salmon red, microscopic crystals, melting quietly at $223-5^{\circ}$ (uncor.); difficultly soluble in water, but soluble in dilute alcohol. Yield, 2.5 grams from 2 grams quinazolone.

Calculated for $C_{18}H_{17}O_2N_2I$: I, 29.11.

Found: I, 28.82.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY
No. 206.]

p-AMINOBENZONITRILE AND CERTAIN OF ITS DERIVATIVES.

[THIRD PAPER.]¹

BY MARSTON TAYLOR BOGERT AND LOUIS ELBERG WISE.

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In continuing the work on *p*-aminobenzonitrile previously reported² from this laboratory, the authors have prepared and studied the following new compounds: *p*-aminobenzonitrile picrate, *p*-nitrobenzoyl-*p*-aminobenzonitrile, *p*-cyanophenyl urethane, *p*-carbamidophenyl urethane, *p*-cyanophenyl urea, *p*-cyanocarbanilide, di-*p*-cyanocarbanilide, *p*-cyanoxanilamide, oxanilic *p*-cyananilide, *p*-cyanosuccinanilic acid, its silver salt, methyl and ethyl esters, *p*-cyanosuccinanil, *p*-cyanophthalanilic acid, *p*-cyanophthalanil, a formaldehyde condensation product, bromo-*p*-acetaminobenzonitrile, 3-nitro-4-acetaminobenzamide, 3,4-diacetyldiaminobenzonitrile, cyano- α -methylbenzimidazole and the corresponding carbamidomethylbenzimidazole.

Of these compounds, the picrate was obtained by bringing the nitrile and picric acid together in benzene solution; the *p*-nitrobenzoyl derivative, by the action of *p*-nitrobenzoyl chloride upon the nitrile in presence of pyridine. From the aminonitrile and ethyl chlorformate, the cyanophenyl urethane was obtained, whose CN was hydrolyzed to a $-\text{CO.NH}_2$ group by the action of an alkalin solution of hydrogen dioxide. *p*-Cyanophenyl urea could not be prepared from the urethane and ammonia, but was obtained from the hydrochloride of the nitrile and potassium cyanate. From the aminonitrile and phenyl isocyanate, the *p*-cyanocarbanilide resulted; and, with phosgene, the di-*p*-cyanocarbanilide.

¹ Read at the Washington Meeting of the Society, Dec. 29, 1911.

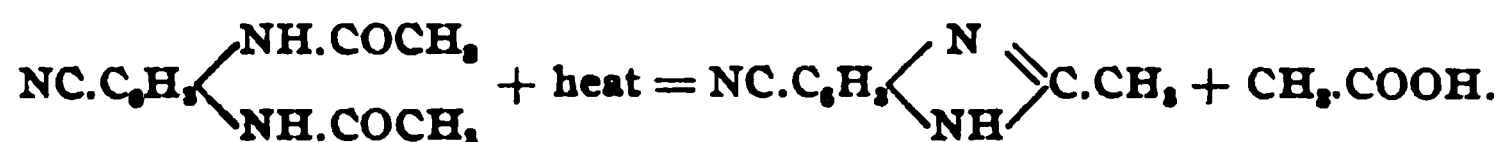
² THIS JOURNAL, 25, 478 (1903); 32, 1494 (1910).

Ethyl *p*-cyanooxanilate and ammonia yielded the corresponding amide, and aniline the anilide. By heating the aminonitrile with the anhydride of succinic or of phthalic acid, the anilic acids were produced, which, on treatment with acetic anhydride, gave the anils.

Formaldehyde condensed with the aminonitrile apparently to a diphen-amine of the structure $\text{CH}_2(\text{NH}.\text{C}_6\text{H}_4.\text{CN})_2$, without the formation of any monomolecular condensation of the type $(\text{CH}_2 : \text{N}.\text{C}_6\text{H}_4.\text{CN})_x$.

Bromination of the acetaminonitrile, like nitration, yielded the mono-substituted product.

From the diacetyldiaminonitrile, the cyanomethylbenzimidazole was obtained by the action of heat, the condensation being accomplished by the elimination of a molecule of acetic acid:



Many of the acids corresponding to the above nitriles have been described by other investigators and will be found in the literature.

Experimental.

p-Aminobenzonitrile was prepared as described in our previous paper,¹ the nitrile being purified by crystallization from water. Instead of attempting to recover the nitrile in the mother liquors by concentration, it was found much more convenient to heat these aqueous mother liquors direct with excess of acetic anhydride, the nitrile being then thrown out in a few minutes as the crystallin acetyl derivative.

Picrate.—1.8 grams of picric acid were dissolved in benzene and a gram of the powdered nitrile added. The mixture was heated for a few minutes, filtered, and the filtrate concentrated. On cooling, the picrate separated in small yellow granular arborescent crystals which, after two re-crystallizations from dilute alcohol, appeared in long, silky, golden yellow needles, melting at 150.5° (cor.), with marked softening about four degrees lower. The substance is easily soluble in hot alcohol, in nitrobenzene or in acetone; moderately soluble in boiling water, in chloroform or in benzene; and very difficultly soluble in ether or in carbon tetrachloride.

Calculated for $\text{C}_{13}\text{H}_9\text{O}_7\text{N}_3$: N, 20.18. Found: N, 20.39.

The following additional information has been gained concerning the solubilities of certain compounds described in our previous papers and may be of service to future workers in this field:

p-Acetaminobenzonitrile is very easily soluble in cold acetone, boiling chloroform, boiling isoamyl alcohol, ethyl acetate, nitrobenzene or hot water; less readily soluble in cold alcohol, glacial acetic acid, or boiling

¹ THIS JOURNAL, 32, 1495 (1910).

isoamyl acetate; moderately soluble in boiling benzene; difficultly soluble in ether; and practically insoluble in carbon tetrachloride.

p-Acetaminobenzamide is readily soluble in boiling water, alcohol or nitrobenzene, crystallizing from the latter on cooling. It is very difficultly soluble in hot benzene, and practically insoluble in boiling ether, acetone or chloroform.

p-Benzoylaminobenzonitrile is easily soluble in cold acetone, hot ethyl or isoamyl alcohols; moderately soluble in cold chloroform, ethyl or isoamyl acetates, or in hot benzene; difficultly soluble in hot water or carbon tetrachloride; and very difficultly soluble in ether.

p-Nitrobenzoyl-*p*-aminobenzonitrile, $O_2N.C_6H_4.CO.NH.C_6H_4.CN$, was obtained from *p*-aminobenzonitrile and *p*-nitrobenzoyl chloride, in presence of pyridine, completing the reaction by a few minutes' boiling, then cooling, and pouring the mixture into a large volume of cold water. The precipitated nitrobenzoyl derivative was filtered out, washed with water and with sodium carbonate solution, and crystallized from 95% alcohol. Long, pale yellow, glistening needles resulted, melting at $258-9^\circ$ (uncor.); readily soluble in hot glacial acetic acid or in nitrobenzene; moderately soluble in cold acetone; rather difficultly soluble in boiling alcohol; very slightly soluble in hot water; and practically insoluble in ether, chloroform or benzene, at their boiling-points.

Calculated for $C_{14}H_9O_2N_3$: N, 15.74. Found: N, 15.83.

p-Cyanophenyl Urethane, $NC.C_6H_4.NHCOOC_2H_5$. The aminonitrile was dissolved in alcohol, the solution diluted, some sodium carbonate added, and then ethyl chlorformate. No action was evident in the cold, but on warming carbon dioxide was evolved and the urethane precipitated in colorless crystals. If sufficient water is not present, some of the product separates as an oil. Treatment of this oil with more water changes it to the crystalline urethane. The product was thoroughly washed with water, re-crystallized twice from dilute alcohol, dried to constant weight, and analyzed:

Calculated for $C_{10}H_{10}O_2N_2$: N, 14.74. Found: N, 15.00.

The pure compound forms colorless, glassy needles, melting at $116-7^\circ$ (cor.), with a faint pineapple odor, and soluble in cold acetone, benzene, methyl or ethyl alcohol, ether or chloroform. In boiling water it first melts to an oil, then slowly dissolves.

p-Carbamidophenyl Urethane, $H_2N.CO.C_6H_4.NHCOOC_2H_5$.—*p*-Cyanophenyl urethane was heated for several hours at 100° with an aqueous solution of hydrogen dioxide (3%) made alkaline with sodium carbonate. The insoluble product was filtered out, washed with a small amount of alcohol, and crystallized thrice from dilute alcohol.

Calculated for $C_{10}H_{12}O_2N_2$: N, 13.46. Found: N, 13.64.

The pure substance crystallizes in slender, colorless, silky needles,

soluble in cold, glacial acetic acid, alcohol, hot benzene, or boiling water; difficultly soluble in boiling ether, acetone or chloroform. The melting point of the compound varies somewhat with the rate of heating. Heated quickly, it melts at about 232.5° (uncor.), but soon thereafter re-solidifies as the temperature rises, with evolution of ammonia. By treatment with chloroform, two substances were separated from this re-solidified melt, one of which remained unfused at 305° (uncor.), and was apparently insoluble in the ordinary solvents, but lack of material precluded further investigation along this line.

Digestion of the urethane with concentrated ammonia, or with a strong (33%) aqueous solution of methylamine, was without effect, no *p*-cyanophenyl urea being formed.

p-Cyanophenyl Urea, $\text{NC.C}_6\text{H}_4\text{.NH.CO.NH}_2$.—The pulverized hydrochloride of *p*-aminobenzonitrile was dissolved in warm water and an aqueous solution of the calculated amount of potassium cyanate added. The urea precipitated immediately. It was filtered out, and purified by treating its aqueous solution with bone-black and re-crystallizing twice from water. The pure compound crystallizes in minute, colorless needles, melting at $207.5\text{--}208.5^{\circ}$ (uncor.); easily soluble in hot ethyl or isoamyl alcohol; soluble in boiling acetone or in hot water; and apparently insoluble in ether, chloroform or benzene.

Calculated for $\text{C}_7\text{H}_7\text{ON}_3$: N, 26.09. Found: N, 26.24.

p-Cyanocarbanilide, $\text{NC.C}_6\text{H}_4\text{.NH.CO.NHC}_6\text{H}_5$.—*p*-Aminobenzonitrile was dissolved in dry benzene and excess of phenyl isocyanate added. As no action appeared in the cold, the temperature was gradually raised to 100° . A yellow, crystalline solid soon separated. The mixture was allowed to stand over night, the precipitate removed, and crystallized from dilute alcohol until the melting point remained constant at 198.5° (cor.). The compound crystallizes in light, feathery clusters of colorless, silky needles, readily soluble in cold acetone, glacial acetic acid or alcohol; soluble in hot benzene or in cold chloroform; slightly soluble in ether; and very difficultly soluble in water. The yield is good.

Calculated for $\text{C}_{14}\text{H}_{11}\text{ON}_3$: C, 70.85; H, 4.68; N, 17.73.

Found:

C, 70.32; H, 4.98; N, 17.37.

These poor results are due in part to the fact that the dry substance was so very light and fluffy that considerable difficulty was experienced in transferring it without loss from the balance to the combustion tube.

Di-p-cyanocarbanilide, $(\text{NC.C}_6\text{H}_4\text{.NH})_2\text{CO}$.—The aminonitrile was dissolved in dry benzene and a benzene-toluene solution of phosgene added. A yellow precipitate separated almost immediately. The mixture was left over night, and the precipitate then filtered out and crystallized from dilute alcohol, from which it separated in small, colorless needles, melting at 273° (uncor.), with slight previous softening, soluble in hot alcohol;

difficultly soluble or insoluble in water, chloroform or ether. Yield, only fair.

Calculated for $C_{10}H_{10}ON_4$: N, 21.38. Found: N, 21.28.

p-Cyanooxanilamide, $NC.C_6H_4.NH.CO.CO.NH_2$.—Ethyl *p*-cyanooxanilate was warmed for a half hour with excess of concentrated ammonium hydroxide solution, then diluted with water and allowed to stand over night. The colorless, crystallin solid was filtered out, and crystallized from glacial acetic acid, giving minute, colorless crystals, melting above 300° , soluble in hot nitrobenzene; very slightly soluble in boiling alcohol; and practically insoluble in water, ether, chloroform, isoamyl acetate or benzene.

Calculated for $C_{10}H_9O_2N_3$: N, 22.23. Found: N, 22.32.

Oxanilic-p-Cyanoanilide, $NC.C_6H_4.NH.CO.CO.NHC_6H_5$.—Ethyl *p*-cyano-oxanilate was boiled for about 15 minutes with aniline and zinc chloride. When cold, the solidified melt was extracted with boiling alcohol. From the alcoholic extracts, crystals were obtained which were purified by dissolving them in boiling glacial acetic acid, filtering, and carefully diluting the filtrate with water. On cooling, crystals separated which were then crystallized from alcohol. As thus purified, the compound forms minute, colorless crystals, melting at 246° (uncor.); soluble in cold chloroform, but practically insoluble in water or ether.

Calculated for $C_{11}H_{11}O_2N_3$: N, 15.85. Found: N, 15.93.

p-Cyanosuccinanilic Acid, $NC.C_6H_4.NH.CO.CH_2.CH_2.COOH$.—Four grams *p*-aminobenzonitrile and 3.5 grams freshly distilled succinic anhydride were brought together in chloroform solution and the whole boiled for half an hour. A crystallin precipitate gradually separated. The mixture was allowed to cool, the precipitate removed, and the filtrate boiled again. Another crop of crystals was obtained, which was removed and the filtrate again heated. This was continued so long as any additional product was obtained. The various crops of crystals, combined and washed with ether or chloroform, amounted to 4.6 grams and were practically pure. Recrystallized from water, the compound forms colorless minute prisms, melting at $213-214^\circ$ (uncor.); soluble in acetone, hot alcohol, boiling water or glacial acetic acid; insoluble in ether, chloroform or benzene.

Calculated for $C_{11}H_{10}O_3N_2$: N, 12.85. Found: N, 12.94.

It is easily soluble in aqueous solutions of ammonia or of the alkali carbonates, and gives a deep, reddish brown solution with ferric chloride, which, after heating for a short time and cooling, precipitates a brown iron salt.

Silver Salt.—The acid was dissolved in a slight excess of ammonium hydroxide solution, the solution warmed, silver nitrate added in excess, and the solution boiled to expel excess of ammonia. On cooling, the

silver salt separated in faintly colored needles, and another crop, of colorless and purer crystals, was obtained from the mother liquor. The salt is easily soluble in ammonium hydroxide solutions, slightly soluble in hot water but practically insoluble in cold.

Calculated for $C_{11}H_9O_2N_2Ag$: Ag, 33.20. Found: Ag, 33.36.

Methyl Ester.—The acid was esterified by suspending it in absolute methyl alcohol and passing in dry hydrogen chloride gas until complete solution resulted, and then pouring this solution upon cracked ice. The colorless, crystalline precipitate which separated was removed, washed thoroughly with sodium carbonate solution, then with water, and recrystallized from dilute methyl alcohol, giving delicate, lustrous, pearly leaflets, melting at $155-156^\circ$ (cor.) with very slight previous softening; easily soluble in cold chloroform or acetone; soluble in hot methyl alcohol, in boiling water or ether; apparently insoluble in the lower petroleum fractions.

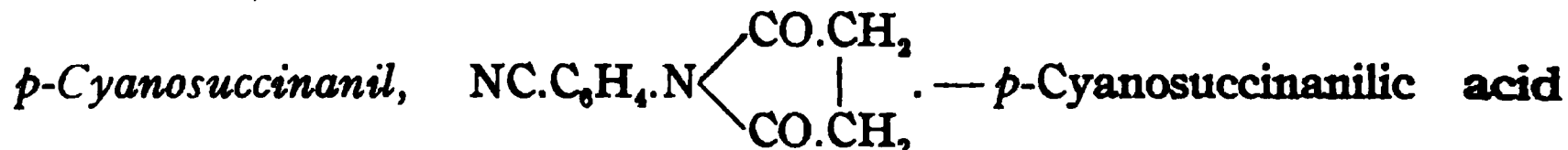
Calculated for $C_{12}H_{11}O_2N_2$: N, 12.07. Found: N, 12.24.

The *Ethyl Ester*, prepared in a similar manner, crystallizes from very dilute alcohol in colorless shining scales, melting at 111° (cor.); readily soluble in chloroform or acetone; soluble in alcohol, ether or hot benzene; insoluble in petroleum ether.

Calculated for $C_{14}H_{13}O_2N_2$: N, 11.38. Found: N, 11.54.

In preparing this ester, if too large an amount of alcohol is used in the esterification, the product is not precipitated when the solution is poured upon cracked ice.

In the course of these esterifications, the formation of imino esters, or of esters of bibasic acids, was not observed.



was added to excess of hot acetic anhydride, and the resulting solution evaporated to small volume. Some water was added, the mixture heated, filtered hot, and from the filtrate on cooling the anil separated in large crystals. Recrystallized repeatedly from water, opaque, ivory colored, coarse crystals were obtained, melting at 170° (cor.); soluble in cold acetone or chloroform, boiling alcohol, hot water, benzene, glacial acetic acid, isoamyl acetate or isoamyl alcohol; apparently insoluble in ether.

Calculated for $C_{11}H_8O_2N_2$: N, 14.00. Found: N, 14.05.

p-Cyanophthalanilic Acid, $NC.C_6H_4.NH.CO.C_6H_4.COOH(o-)$.—3.1 grams phthalic anhydride were dissolved in 50 cc. chloroform, a solution of 2.5 grams *p*-aminobenzonitrile in 25 cc. chloroform added, and the mixture heated to boiling. Nearly colorless, silky needles separated from the boiling solution. On filtering out these needles and boiling the mother liquor, another crop of crystals was obtained; and this was

continued until nothing further separated from the mother liquor on boiling. Total yield, 5 grams. The various crops of crystals were combined and recrystallized from chloroform, giving fine colorless needles, very easily soluble in alcohol or ether; soluble in glacial acetic acid, warm acetone, hot isoamyl acetate, boiling water, boiling benzene or toluene; and appreciably soluble in cold chloroform. When heated sufficiently high, the substance loses water and forms the anil. The melting point, therefore, varies with the rate of heating. If plunged in a bath at 145° , it melts at about 163° , and soon thereafter the anil begins to sublime in the upper part of the tube.

Calculated for $C_{10}H_{10}O_2N_2$: N, 10.53. Found: N, 10.73.

p-Cyanophthalanil, $NC_6H_4.N \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} C_6H_4$, was formed, as just stated,

when *p*-cyanophthanic acid was heated above its melting point. The following, however, was found to be a better method of preparation: The anilic acid was added gradually to an excess of acetic anhydride, the solution evaporated to crystals, excess of anhydride destroyed by warming the crystalline mass with water, and the crude product recrystallized from alcohol. Feathery clusters of colorless silky hairs resulted, melting at 187° (cor.); readily soluble in glacial acetic acid, benzene, toluene, nitrobenzene, chloroform, acetone, boiling ethyl or isoamyl alcohol; soluble in ether or isoamyl acetate; and difficultly soluble in hot water. It sublimes readily and seems to be volatil with steam.

Calculated for $C_{18}H_{12}O_2N_2$: N, 11.29. Found: N, 11.44.

Formaldehyde Condensation Product.—One gram *p*-aminobenzonitrile was dissolved in acetone and about 3 cc. of aqueous formaldehyde solution were added. As nothing precipitated on standing, the solution was concentrated and water added. A syrupy sticky mass settled out, over which was a layer of fine colorless needles. When the sticky mass was boiled with water, practically all of it dissolved and, on cooling, more of the colorless needles were obtained. These needles were recrystallized several times from water, then dissolved in acetone, reprecipitated with water, and dried in a vacuum. They then melted at about 158° (uncor.), and under the microscope appeared as fine colorless hairs. The substance is easily soluble in acetone, hot alcohol or boiling chloroform; soluble in hot, but very difficultly soluble in cold water.

Calculated for $C_{18}H_{12}N_4$: N, 22.58. Found: N, 22.21, 22.60.

This would correspond to a methylene di(*p*-cyanophenamine) of the structure $CH_2(NH.C_6H_4.CN)_2$.

Under similar conditions, using anthranilic nitrile, Grube¹ obtained a derivative of the type $(CH_2 : N.C_6H_4.CN)_x$.

¹ *Inaug. Dissert., Marburg, 1909.*

Bromo-p-acetaminobenzonitrile, $(4)CH_3CONH.C_6H_4Br.CN(1)$.—*p*-Acetaminobenzonitrile was dissolved in warm, moderately strong acetic acid, excess of bromine added gradually, the mixture let stand over night, and excess of bromine then removed by boiling. The solution was largely diluted with water and the precipitated bromo compound crystallized repeatedly from 95% alcohol. The compound crystallizes in colorless glassy needles, occasionally united in rosets, melting at $161.5-162.5^\circ$ (cor.), easily soluble in hot alcohol, in chloroform, acetone or glacial acetic acid; slightly soluble in boiling ether or carbon tetrachloride; difficultly soluble in water. The location of the bromine was not determined.

Calculated for $C_8H_7ON_2Br$: N, 11.72; Br, 33.44. Found: N, 11.80; Br, 33.99.

3-Nitro-4-acetaminobenzamide, $CH_3CONH.C_6H_3(NO_2).CONH_2$.—3-Nitro-4-acetaminobenzonitrile was heated for an hour or two with an alkaline hydrogen dioxide solution (3%). A small amount of acetic anhydride was added, to reacetylate any nitroaminonitrile formed, and the whole evaporated to dryness. The residue was washed thoroughly with water and crystallized from alcohol, giving lustrous yellow scales. On further recrystallization from alcohol, flat, yellow, branching needles were obtained instead of scales. These needles softened and sublimed at about 215° , finally melting at 239.5° (uncor.) in a sealed capillary tube.

Calculated for $C_9H_6O_4N_2$: N, 18.84. Found: N, 18.84.

The compound is soluble in hot, less so in cold alcohol; very slightly soluble in boiling chloroform; appreciably soluble in boiling water; and apparently insoluble in cold water, cold chloroform, boiling benzene or boiling ether. Heated with aqueous potassium hydroxide, it yields the nitroaminobenzoic acid.

Thieme¹ endeavored to prepare this amide by the action of aqueous or of alcoholic ammonia upon the nitroacetaminobenzoic ester, but was unsuccessful, the acetyl group being split off each time.

3,4-Diacetaminobenzonitrile, $(CH_3CONH)_2C_6H_3.CN$.—The diaminonitrile was treated with acetic anhydride and the solution warmed. A colorless precipitate soon separated. Water was then added and the mixture boiled, to destroy excess of acetic anhydride and to dissolve the crude acetyl derivative. The solution was filtered hot and from the filtrate on cooling, the acetyl derivative crystallized. It was purified by repeated recrystallization from water, decolorizing with bone-black, and then appeared as colorless, silky hairs, soluble in glacial acetic acid, alcohol or boiling water; difficultly soluble in hot chloroform or in benzene; practically insoluble in ether.

Calculated for $C_{11}H_{11}O_4N_3$: N, 19.35. Found: N, 19.17.

The pure substance melts at $238-238.5^\circ$ (uncor.), and in the neighbor-

¹ *J. prakt. Chem.*, [2] 43, 457 (1891).

hood of 240° loses acetic acid with formation of the cyanbenzimidazole. If heated to $250-60^{\circ}$, charring results.

Cyano- α -methylbenzimidazole, $\text{NC.C}_6\text{H}_4\text{C}(\text{NH})\text{N.C.CH}_3$.—The preparation

of this imidazole was attempted by the following methods:

1. By reduction of 3-nitro-4-acetaminobenzonitrile. Reduction with stannous chloride and hydrochloric acid gave only the diaminobenzonitrile.

2. By the action of acetic acid on the diaminobenzonitrile.—0.53 gram of the crude diaminonitrile was boiled for an hour and three-quarters with a large excess of glacial acetic acid. The excess of acid was then partly removed by distillation and the residual solution made alkaline with sodium carbonate. A nearly colorless product separated. This was collected with ether, in which it dissolves with difficulty, and the ether then driven off. The residue was purified by repeated crystallization from water, and formed a colorless granular solid, melting at 241° (uncor.). Yield, 0.099 gram.

Calculated for $\text{C}_9\text{H}_7\text{N}_3$: N, 26.76. Found: N, 26.33.

This result is fairly good considering the very small amount available for analysis.

3. By the action of heat on 3,4-diacetaminobenzonitrile.—By carefully heating the diacetaminonitrile, it loses acetic acid in the vicinity of 240° , as before mentioned, and from the residue there was isolated a substance, crystallizing from water in granules and melting at 241° (uncor.).

Calculated for $\text{C}_9\text{H}_7\text{N}_3$: C, 68.75; H, 4.49; N, 26.76.

Found: C, 68.19; H, 4.63; N, 26.55.

The imidazole, as prepared by the above methods, is usually in dull granular clusters of microscopic crystals, or occasionally in opaque needles. It sublimes as a glistening, tinsel-like deposit, and is readily soluble in acetone, glacial acetic acid, boiling water or amyl acetate; moderately soluble in alcohol; difficultly soluble in ether or chloroform; and apparently insoluble in carbon tetrachloride.

Carbamido- α -methylbenzimidazole, $\text{H}_2\text{NCO.C}_6\text{H}_4\text{C}(\text{NH})\text{N.C.CH}_3$. — As

Hübner¹ succeeded in obtaining methylbenzimidazole from *o*-nitroacetanilide by reduction with tin and glacial acetic acid, we tried the same reducing agents on the nitroacetaminobenzonitrile, except that we found the reduction to proceed apparently more efficiently with a diluted acid instead of the glacial. After heating for nine and a quarter hours with the reducing agents, the mixture was cooled and filtered, and the

¹ *Ann.*, 209, 353 (1881).

red filtrate made slightly alkaline with potassium hydroxide. A small amount of dark precipitate separated and was removed. The filtrate was treated carefully with acetic anhydride, and a nearly colorless crystalline substance separated, soluble in excess of acetic anhydride. Recrystallized twice from water, after treatment with bone-black, and then twice from alcohol, it formed colorless needles, decomposing at about 270° (uncor.). Heated with concentrated potassium hydroxide solution, ammonia was evolved.

Calculated for $C_9H_8ON_2$: C, 61.68; H, 5.18; N, 24.00.

Found: C, 61.70; H, 4.53; N, 24.44, 24.57.

These results, although the hydrogen and nitrogen figures are rather wide of the mark, seem to indicate that the substance is the carbamidomethylbenzimidazole. It is soluble in hot water, in alcohol or glacial acetic acid; and difficultly soluble or insoluble in ether, chloroform or benzene.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE ACTION OF IODIDES ON BROMANIL. IODANIL AND SOME OF ITS DERIVATIVES.¹

BY H. A. TORREY AND W. H. HUNTER.

Received March 18, 1912.

The work described in this paper was started with the intention of preparing some tetrahalogen derivatives of benzoquinone, having both bromine and iodine in the molecule, and studying the reactivity of the different halogens.² Data have been collected along two main lines: the study of the products of the reaction between potassium or sodium iodide and bromanil, and a preliminary study of the hitherto unknown iodanil. Use was made of both potassium and sodium iodide to effect the replacement of bromine by iodine, and both ethyl alcohol and acetone were used as solvents. Our use both of sodium iodide and of acetone was quite independent of the work of Finkelstein,³ and as a matter of fact antedated its publication.

The addition of solid potassium iodide to a cold acetone solution of pure bromanil resulted in the setting free of iodine, and the formation of a green compound, which was rapidly destroyed if the solution was

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy by William Hammett Hunter.

This research was suggested by the late Professor H. A. Torrey, and the experimental work was carried on under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

² Prel. notice in *Ber.*, 38, 555 (1905).

³ *Ber.*, 43, 1528 (1910).

heated. This green substance was due to an independent reaction and bore no relation to the bromoiodoquinones formed by heating the mixture, except that the reduction of a portion of the quinone removed it from the sphere of the subsequent action. When the mixture was heated, the principal product was brown, and melted at about $255-6^{\circ}$. It gave, on analysis, numbers corresponding closely with the theory for a dibromodiiodoquinone.

Further work after the publication of the preliminary notice showed that if large quantities were taken, the product had a much higher melting point. Crystallization experiments on an extended scale showed that this was not due to bromanil, which was absent. A fractionation led to three fractions, of melting points $276-282^{\circ}$, $255-259^{\circ}$, $256-61^{\circ}$. Analyses of these fractions showed that the first was composed of nearly pure tetraiodoquinone, the precipitate from the Carius determination showing on electrolysis in potassium cyanide that it was practically pure silver iodide. The second fraction was a mixture, probably of iodanil, dibromodiiodoquinone and bromotriiodoquinone, while the third fraction was almost pure dibromodiiodoquinone, showing that not only two, but all of the bromine atoms of bromanil could be replaced by iodine.

It was found that iodanil could be made the principal product of the reaction by heating first with potassium iodide, and next, with sodium iodide in alcohol. Prepared in this way, iodanil is a very dark brown substance, melting at $284-286^{\circ}$ with evolution of iodine. Its color shows the strong deepening effect exerted by the replacement of chlorine or bromine by iodine. It crystallizes in needles, while chloranil and bromanil crystallize in thin plates, though dibromodiiodoquinone could be made to crystallize either in plates or needles.

A number of interesting derivatives of iodanil were prepared, for purposes of comparison with bromanil and chloranil. The reactions were chosen chiefly from some studied in the Harvard laboratory by Jackson and Grindley.¹

As a result of the preparation of diiododiphenoxyquinone, and the diparacresoxy compounds from all three quinones, we were able to study the influence of the composition of these substances on their melting points, as shown in the following table.

	Diphenoxy.		Diparacresoxy.
Dichlor.....	243°	(Jackson and Grindley)	$254-5^{\circ}$
Dibrom.....	$266-7^{\circ}$	" "	$262-3^{\circ}$
Diiod.....	290°		$272-4^{\circ}$ (sl. dec.)

In each case, the melting point of the bromine compound is almost exactly the mean of the melting points of the other two.

Other reactions studied were the formation of hemiacetals by sodium

¹ *Proc. Am. Acad.*, 409 (1894).

alcoholates on the quinone, which also led to the formation of the very interesting iodoanilic acid, and the action of aniline on the diiododiphenoxy quinone. In the latter case we found not only a replacement of phenoxy by anilino groups, but of iodine by hydrogen as well, giving dianilinoquinone and the monoanil of monoiododianilinoquinone. This result was not unexpected, as we had already found that aniline on dibromodiiodoquinone gave us dianilinoquinone and probably monobromodianilinoquinone. This is a case of the replacement of halogen by hydrogen in benzene derivatives, a reaction being studied by Professor Jackson, who has previously found many instances of it, some of which are noted in the introduction to his paper with Grindley.

The study of the derivatives of iodanyl has been continued in this laboratory, and a considerable quantity of material is now ready for publication.

Although bromotriiodoquinone was isolated from iodanyl mother liquors, it is so difficult to obtain in quantity in a pure state that little work could be done on it. It crystallizes in short, brown, prismatic needles, melting at $253-4^{\circ}$. It gives, with sodium phenolate, monobromomonoiododiphenoxyquinone, of melting point $282-283^{\circ}$, which is identical with the compound obtained before from dibromodiiodoquinone and described as melting at $281-282^{\circ}$.

The formation of the same bromoiodoquinone from these two quinones is certainly unexpected, if the phenoxy groups always enter in the 2,5-position, as has been supposed, because it would certainly be expected that the iodine atoms in dibromodiiodoquinone would be in the 2,5-position also. The most probable explanation is that in the early part of the work, while trying to make some of the diiodo compound, we actually hit on the triiodo compound instead. This might easily have happened, as at that time it was not known that more than two atoms of bromine could be removed from bromanil by potassium iodide, and the melting point of the triiodo compound is so close to the melting point of dibromodiiodoquinone, that it would have been impossible to distinguish the two by this single property. If this is not the explanation, we are forced to believe that the replacement of bromine by iodine takes place on differently placed ring atoms than that of halogen by the phenoxy groups, or that the iodine atoms are not para to each other in dibromodiiodoquinone. Either of these suppositions is out of harmony with our knowledge of quinones up to the present time, so it seemed important to us to prepare a diphenoxy derivative from undoubted dibromodiiodoquinone. The preparation of this compound in a pure state unfortunately succeeded only at the close of our work together, and as a result we are unable to make any final statement in regard to the action of sodium phenolate on dibromodiiodoquinone.

Dibromodiiodoquinone is obtained as a light brown compound, crystallizing in needles if slowly cooled but in plates if cooled rapidly. It melts at 258–259° in a pure state, instead of at 255–256°, as given in the preliminary notice.

The replacement of bromine by iodine is not the only effect of potassium iodide on bromanil. It has already been mentioned that on mixing the solid, finely ground potassium iodide with the bromanil in acetone, a green substance was formed, if the solution was cold. Chloranil gave an identical action, and sodium iodide in acetone readily gave precipitates with chloranil, bromanil, tetrabromo-*o*-quinone, and tetrachloro-*o*-quinone. The potassium derivative from chloranil and the sodium derivatives from chloranil and tetrabromo-*o*-quinone were analyzed, and indicated that they were the alkali salts of the unknown octohalogen quinhydrones. This result was confirmed by the action of dilute sulfuric acid on the sodium salt from chloranil, which gave chloranil and tetrachlorohydroquinone. We actually had, therefore, salts analogous to those of known quinhydrones described by Jackson and Oenslager.¹

The question as to why the salts of these quinhydrones should be stable, when the free quinhydrones are unknown, is an interesting one. Ling and Baker² found that they could get a hexachloroquinhydrone, but not an octochloro compound, and decided that the stability is in inverse proportion to the number of halogen atoms, but that this cannot be the only condition influencing stability is shown by the existence of our salts. Hardenbergh³ and one of us found that quinhydrone and phenanthroquinone are dissociated in solution in accordance with the reversible equation



Ling and Baker point out that the lower halogenated quinhydrones are insoluble in cold alcohol, while the higher members are soluble. It would seem, then, that the question of the formation or non-formation of a given quinhydrone may be a function of the solubility of its factors and of the compound itself. Just as Hardenbergh and one of us were able to throw out quinhydrone⁴ from solutions by addition of either factor, so addition of a great excess of a factor might throw out a quinhydrone which did not precipitate on the usual mixing of equal molecules. The octochloroquinhydrone should be fairly soluble, while chloranil and tetrachlorohydroquinone are not very soluble, and this is probably why Ling and Baker could not obtain the quinhydrone. So the stability of

¹ *Am. Chem. J.*, 18, 4 (1896).

² *J. Chem. Soc.*, 63, 1314 (1893).

³ *Am. Chem. J.*, 33, 167 (1905).

⁴ *Loc. cit.*

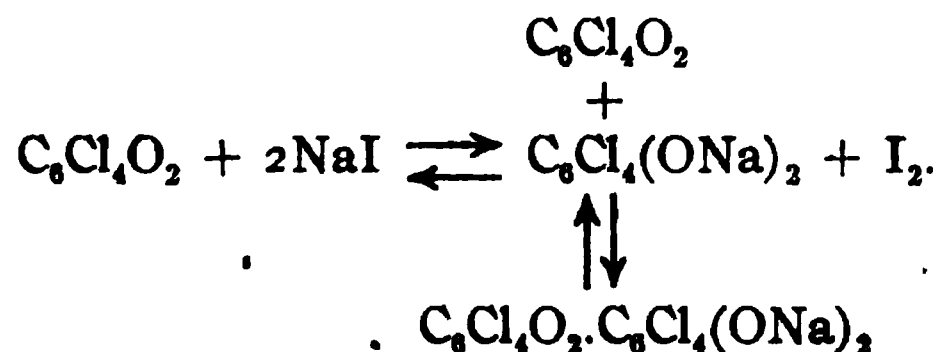
the halogenated quinhydrones may be considered to depend on the number of halogens present only as this affects the solubility of the factors and of the quinhydrone itself.

For instance, in the present case, the green salt is so insoluble that the solutions of chloranil and iodide need only be mixed to cause the precipitation, but a far greater yield is obtained with the more soluble sodium iodide than with potassium iodide.

The relation between the reduction reaction and the substitution reaction is also interesting. The reduction reaction, best shown by chloranil, is a balanced one:



At low temperatures, the equilibrium is far to the right, on account of the precipitation of green salt, but at high temperatures the dissociation of the quinhydrone salt and the oxidizing effect of the iodine increase together, driving it back to the quinone, which then reacts with the sodium iodide to substitute iodine for chlorine or bromine. A complete picture of the equilibria in the reduction is then given by the scheme



That the reactions are independent is shown by two facts. Cold, 95% alcohol as solvent does not lead to the formation of green salt, but on standing months, gives the substitution reaction. This shows the effect of non-formation of green salt in allowing the other reaction to occur. The other point showing the independence of the reactions is that in a regular preparation of iodoquinones, the iodine set free accounted for all the bromanil which did not appear as iodoquinones, showing that the formation of the iodoquinones is not connected with the formation of green salt, which is a secondary reaction, in consequence of the reduction of part of the quinone.

Experimental Part.

Bromanil was prepared by a modification of the method of Ling:¹ 20 grams of hydroquinone were suspended in glacial acetic acid, and 175 grams of bromine (6 mol.) were added. After standing over night, an equal volume of water and some concentrated nitric acid were added and the mixture heated on the steam bath till bromine was no longer evolved. The nitric acid liberates bromine from the hydrobromic acid present, and a more complete bromination occurs. The bromanil

¹ *J. Chem. Soc.*, 61, 568 (1892).

was crystallized from glacial acetic acid, and a product melting at 290° or over was used for our work. Pure bromanil melts at 300° ¹ and it was shown by analysis that about 2.5% of tribromoquinone lowered the melting point about 25° .

Action of Potassium Bromide in Hot Alcohol on Bromanil.—Twenty grams of bromanil were heated two hours with 20 grams finely ground potassium iodide in alcohol, under a reflux condenser. The product was fractionated, using ethyl acetate as solvent. Three fractions resulted, of the following melting points and composition:

(A) Most insoluble. Melting point, $276-282^{\circ}$.

Calculated for $C_6I_4O_2$: I, 83.00. Found: 83.90, 83.78.

The precipitate from the second analysis on electrolysis gave: Ag = 46.08%. AgI requires 45.95% Ag.

(B) Melting point, $254-6^{\circ}$. Calculated precipitate as AgBrAgI.

Calculated for $C_6Br_2I_2O_2$: Br + I = 79.92. Found: 78.65, 78.13.

Calculated precipitate as AgBr₂AgI.

Calculated for $C_6BrI_3O_2$: Br + I = 81.58. Found: 83.00, 82.55.

(C) Most soluble fraction. Melting point, $255-9^{\circ}$.

Calculated for $C_6Br_2I_2O_2$: Br + I = 79.92. Found: 80.23, 80.24.

From these data it is obvious that instead of dibromodiiodoquinone only, as stated in the preliminary paper, potassium bromide gives with bromanil bromotriiodoquinone and iodanil as well. Methods were found for isolation of all three, as follows:

Dibromodiiodoquinone.—This was found to be the principal product, in the following conditions:

Ten grams of bromanil and 7.8 grams of potassium iodide (2 mol.) were heated two hours under a reflux condenser with 100 cc. of alcohol. The reaction mixture was then poured into water, filtered, and the brown precipitate washed with water and alcohol. Careful crystallization from ethyl acetate gave a substance of melting point constant at $258-59^{\circ}$, with slight sublimation. Analyzed for halogen.

Calculated for $C_6Br_2I_2O_2$: Br + I = 79.92.² Found: 80.49.

This checks with the results in the preliminary notice; found: 79.79, 79.76.

One of these precipitates had been analyzed for silver by the method of Mansel,³ solution in thiosulfate, and precipitation by ammonium sulfide.

Calculated for AgBrAgI: Ag, 51.30. Found: 51.09.

¹ Graebe and Weltner, *Ann.*, 263, 33 (1891).

² Calculations of these analyses were made by separate calculations for each possible ratio of bromine and iodine. This led to better results than the "indirect" method, which led in the case mentioned above to wide variations from the theoretical, though the silver determination checks the composition fairly closely.

³ *Z. anal. Chem.*, 9, 208 (1870).

Analysis for carbon and hydrogen. Silver spirals and "molecular" silver were necessary to hold back iodine.

Calculated for $C_6Br_2I_2O_2$: C, 13.91; H, 0.0.

Found: (I) C, 13.95; H, 0.15.

(II) C, 14.25; H, 0.30.

Dibromodiiodoquinone is a reddish brown substance, melting at $258-9^\circ$. It crystallizes from ethyl acetate in plates on rapid cooling, and in deep red brown prismatic needles on cooling slowly. It is more soluble than iodanil, but less than bromanil, in all other solvents. It is soluble in ethyl acetate, benzene, acetone, glacial acetic acid, less soluble in alcohol, chloroform, ether, and ligroin. Reduction by sulfur dioxide in acetone and water gave a colorless substance, melting, crude, at $243-244^\circ$. The quinone is unaffected by acids, but readily decomposed by alkalis.

Bromotriiodoquinone.—In the mother liquors from the preparation of iodanil, there was obtained a quinone of constant melting point $253-254^\circ$, which was at first supposed to be dibromotriiodoquinone. It proved, on analysis, to be bromotriiodoquinone. $C_6BrI_3O_2$ requires $Br + I = 81.58\%$. Found: 81.44, 81.24.

It crystallizes in rather short, broad, prismatic crystals, rich brown in color, intermediate in solubilities between iodanil and dibromodiiodoquinone. It melts within less than a degree. Sodium phenylate reacts with it to form bromiododiphenoxyquinone.

Iodanil.—Fifteen grams of powdered bromanil were treated with 11.7 grams (2 mol.) of potassium iodide in 150 cc. of alcohol. The yield was poor if larger amounts were used. The mixture was heated two hours on the steam bath with a reflux condenser, and cooled rapidly, filtered with suction, and the red brown substance filtered with suction and washed with alcohol and water. It was then replaced in the flask with 10.6 grams (2 mol.) of sodium iodide and 150 cc. of alcohol, and heated two hours more. The substance rapidly became dark brown. It was isolated by filtration and washing free of iodine, and recrystallized from ethyl acetate till it showed the constant melting point $282-284^\circ$. It is a slow process to raise the melting point above 270° , apparently because of formation of mixed crystals. Sodium iodide must be used in the second part of the heating, as potassium iodide leads to the formation of a purple compound containing potassium, which is not further acted on.

Iodanil crystallizes in small chocolate colored needles, melting at $282-284^\circ$ with evolution of iodine. It is slightly soluble in benzene, glacial acetic acid, acetone and cold ethyl acetate, fairly soluble in hot ethyl acetate; practically insoluble in the other common solvents. Acids have no action, but alkalis evidently produce a deep seated change.

Derivatives of Dibromodiiodoquinone.

Action of Amines.—An addition product with diphenylamine of the type studied in this laboratory by Jackson and Clarke¹ was prepared as follows: A large excess of diphenylamine was dissolved in ligroin and powdered dibromodiiodoquinone, which is only slightly soluble in ligroin, was allowed to stand in this solution until it had all become converted into the fine purplish black needle-like crystals of the addition product, which was filtered off and washed with a little ligroin. It resembled in every way the compounds described by Jackson and Clarke, and so proved the quinone nature of our compound. It melted over a wide range of temperatures, according to the speed of heating, and was decomposed by most solvents, leaving the quinone. The dry substance gave a green powder on grinding. It was placed in a desiccator over hard paraffin until analyzed.

Calculated for $C_6Br_2I_2O_2 \cdot (C_6H_5)_2NH$: Br + I = 60.23. Found: 60.31.

Action of Potassium Phenolate.—Bromoiododiphenoxyquinone was prepared by treating 1.5 grams of the powdered dibromodiiodo quinone with a solution of 0.3 gram caustic potash and 0.6 gram phenol (= 2 mol. potassium phenolate), and heating two hours on the steam bath with a reflux condenser. A salmon colored substance resulted, which was filtered off, and washed well with water. Both bromine and iodine salts were found in the filtrate. It was crystallized from toluene till it showed a constant melting point, 281–282°. (This melting point was raised to 282–283° when the substance was prepared from bromotriiodoquinone.) In the mother liquors was found a small amount of a red substance, melting at 227–231° after two crystallizations, which was probably the tetraphenoxyquinone described by Jackson and Grindley, who give the melting point as 229–230°. The diphenoxy compound was analyzed for halogen.

Calculated for $C_6BrI(OC_6H_5)_2O_2$: Br + I = 41.62. Found: 41.62, 42.16.

The substance was shown to contain both bromine and iodine by decomposition with strong caustic soda, and application of the usual tests. It melts at 282–283°, with sintering just before melting. It is soluble in ethyl acetate, benzene, and toluene, the last being an excellent crystallizing medium for it. It is somewhat soluble in alcohol, ether, and acetone, almost insoluble in ligroin. Acids are without effect, but alkalis decompose it, first splitting off the phenoxy groups.

Action of Aniline.—Some dibromodiiodoquinone was dissolved in toluene, a large excess of aniline added, and the mixture boiled for an hour under a reflux condenser. The solution turned brown, a thick precipitate appeared and, on cooling, the liquid almost solidified. Crystallization from toluene separated the precipitate formed into two compounds,

¹ *Am. Chem. J.*, 34, 441 (1905).

a plum colored and a yellow substance. The plum colored compound is almost insoluble in toluene and was identified as dianilinoquinone by crystallization from hot nitrobenzene, analysis, and by comparison with a known sample, made by the method of A. W. Hofmann.¹

Calculated for $C_{12}H_8(NHC_6H_5)_2O_2$: N, 9.66. Found: 9.28, 9.37.

The yellow compound crystallized from toluene abundantly, in the form of fine yellow needles. It was recrystallized several times, but as it did not melt at 300° , it was hard to decide as to its purity. Three different samples gave varying halogen contents, and but one nitrogen determination had been made when it became necessary to end the work.

Calculated for $C_{12}H_7Br(NHC_6H_5)_2O_2$: Br, 21.66; N, 7.61.

Found:

Br, 19.18, 23.90, 21.89; N, 7.69.

There was no iodine in the precipitate from the first halogen analysis. It seems safe, therefore, to consider that the substance formed was bromo-dianilinoquinone.

The Action of Potassium Phenolate on Bromotriiodoquinone.—One and one-half grams of pure substance were heated an hour and a quarter with a solution of two molecules of potassium phenylate. The diphenoxy compound resulting was then filtered, washed, and crystallized from toluene, when it showed the constant melting point $282-283^\circ$, hence, was the bromiododiphenoxyquinone described before, as the dibrom compound melts at $266-267^\circ$, and the diiodo compound at 290° .

Derivatives of Iodanil.

Action of Phenolates.—Two and one-half grams of iodanil were treated with a little over two molecules of sodium phenolate, dissolved in 25–30 cc. of water, and the mixture heated an hour on the steam bath. The salmon colored precipitate formed was washed with water, then with alcohol, and dried. After crystallization from toluene it reached the constant melting point 290° .

Calculated for $C_{12}I_2(OC_6H_5)_2O_2$: I, 46.67. Found: 46.42.

The precipitate gave a negligible extract on three days' treatment with strong ammonia.

The diiododiphenoxyquinone resembles the other diphenoxy compounds in color and solubilities. It differs in its reactivity to sodium hydroxide, as it does not give iodanilic acid on warming, but instead, ether extracts from the filtered and acidified solution give a yellow compound, which may, perhaps, be the mono ether. It was not investigated.

The Action of Cresolates.—It was thought worth while to try the action of the different cresolates on iodanil, and their action was tried on bromanil and chloranil also. *o*-Cresolates were found to give much black tar; the *m* compounds were more like the phenolates, though a compound was isolated only from bromanil. The *p*-cresolate worked

¹ *Jsb.* (1863), 413.

very smoothly, in the same manner as the phenolate. The cause of the difference may be that the methyl groups are attacked in some way by the quinone, leading to the formation of the tarry products. The method used was identical with that for the phenolates, save that where tar was formed, it was removed with alcohol, in which the cresoxy compounds are not very soluble.

Dibromodi-m-cresoxyquinone.—Fine, salmon red needles from benzene-ligroin. Melting point constant at 193° .

Calculated for $C_8Br_2(OC_6H_4OCH_3)_2O_2$: Br, 33.46. Found: 33.8.

Much more soluble in all solvents than the diphenoxy compounds.

Dibromodi-p-cresoxyquinone.—Salmon colored needles from toluene, melting at 254° with decomposition on slow heating, at $262-263^{\circ}$ with decomposition on rapid heating.

Calculated: Br, 33.46. Found: 33.07.

Dichlorodi-p-cresoxyquinone.—It was necessary here to moisten the chloranil with dilute acetone before adding the cresolate solution, which was made up with 1 : 2 caustic potash, and only five minutes' heating was necessary. Melting point from toluene, $254-5^{\circ}$, with rapid heating.

Calculated for $C_8Cl_2(OC_6H_4CH_3)_2O_2$: Cl, 18.11. Found: 18.23.

Diiododiparacresoxyquinone.—Heated one hour, concentrated cresolate solution. Melting point became constant at $272-274^{\circ}$, with blackening at 269° , and evolution of iodine.

Calculated: I, 44.38. Found: 44.89.

Sodium Alcoholates on Diiododiphenoxyquinone, Diiododiethoxyquinone-diethylhemiacetal.—One and four-tenths grams of diiododiphenoxyquinone were treated with a little over four atoms of sodium dissolved in 20 cc. of absolute alcohol. The reaction started immediately, and was allowed to continue with stirring and breaking up of the diphenoxy compound, until all the red color of the latter had disappeared. There was then present a white precipitate of the sodium salt of the hemiacetal, as was found by Jackson and Grindley in their work.¹ This was not isolated, but dissolved by adding the requisit water. The filtered solution was then acidified with dilute sulfuric acid and the white granular precipitate of the hemiacetal was filtered, washed well with water till the wash-waters were colorless; then dissolved in dilute caustic soda and reprecipitated, filtered and washed. This alternate precipitation and solution was continued until the precipitate collected was white. Much iodanilic acid was formed from the hemiacetal during this purification, as was shown by the purple color of the solutions and wash waters, and a considerable amount of it was recovered from the wash waters. The hemiacetal was pure white, as viewed in the clear liquid, but when collected,

¹ *Proc. Am. Acad.*, 29, 432 (1894).

it was faintly yellow. It was air dried, brought to constant weight *in vacuo*, and analyzed.

Calculated for $C_6I_2(OC_2H_5)_2(OH, OC_2H_5)_2$: I, 47.01. Found: 46.81 per cent.

It was possible to obtain this hemiacetal in minute crystals by evaporation of its solutions. No other member of the class has been obtained in crystallin form. It is somewhat soluble in cold alcohol, less in the other ordinary solvents. It forms a red compound, presumably diiododiethoxyquinone, on heating with hydrochloric acid on the steam bath, and also on heating the dry hemiacetal in a melting point tube to 140° .

Diiododimethoxyquinonedimethylhemiacetal.—One and one-half grams of diiododiphenoxyquinone were treated with a little over four atoms of sodium, dissolved in 25 cc. of absolute methyl alcohol. No sodium salt was precipitated. The purification was identical with that of the ethyl compound.

Calculated for $C_6I_2(OCH_3)_2(OH, OCH_3)_2$: I, 52.45. Found: 52.46.

This hemiacetal was almost pure white. It was somewhat soluble in all the ordinary solvents, but did not crystallize. It lost two molecules of alcohol under the same conditions as did the ethyl derivative. It was found that the sodium salt could be made from iodanil as easily as from diiododiphenoxyquinone, by the direct action of sodium methylate.

Iodanilic Acid.—This could not be formed as the corresponding chlorine and bromine compounds by the direct action of alkalies on the quinone or on the diphenoxy derivative. Three grams of crude iodanil were treated with an excess of sodium methylate solution. The quinone dissolved. The hemiacetal was isolated as before, and dissolved in considerable *N* caustic soda. This solution was heated till it just commenced to boil when it turned the color so characteristic of the alkali salts of the "anilic" acids. It was allowed to cool, and the perfectly clear solution was acidified with dilute sulfuric acid, causing a copious precipitate of iodanilic acid. About one or two cc. of concentrated sulfuric acid were then added to complete the precipitation, whereupon the solution turned yellow in a very characteristic manner. The filtered precipitate was washed till the wash water commenced to run through purple, showing the almost complete absence of sulfuric acid. Nine-tenths gram of air-dried acid was obtained. It was purified by crystallization from benzene, whence it was deposited in hard transparent red needle-like crystals, becoming opaque in the air. Dried at 100° .

Calculated for $C_6I_2(OH)_2O_2$: I, 64.78. Found: 65.04.

Part of the crude acid was less soluble in benzene, and proved to be a yellow compound, slightly soluble in water, readily in alkalies. It was, perhaps, the hemiether of iodanilic acid, for it resembled the yellow substance obtained as one product of the action of alkali on diiododi-

phenoxyquinone. It is hoped that the study of these compounds will be continued in this laboratory.

Properties of Iodanilic Acid.—It dissolves in water with the same purple color as chloranilic and bromanilic acids. Strong sulfuric acid precipitates it from concentrated aqueous solution in yellow red feathery crystals, while dilute acids throw down a reddish precipitate. The two precipitates probably differ in content of water, as the chloranilic and bromanilic acids precipitate in hydrated form. Iodanilic acid dissolves in benzene with a yellow red color, presumably corresponding to the anhydrous state. It commences to decompose at about 205° , giving off iodine.

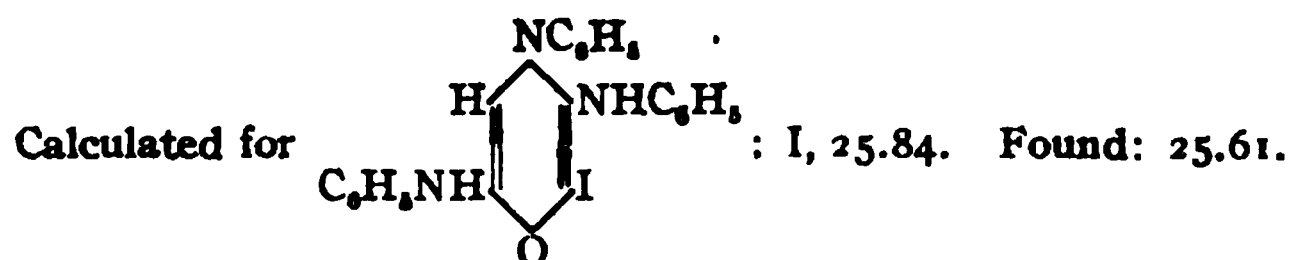
The Action of Aniline on Diiododiphenoxyquinone.—Two grams of the diphenoxy compound were warmed on the steam bath with 10 cc. of aniline for a few minutes, when the color of the diphenoxy compound disappeared. The mixture was cooled and freed from aniline by dilute sulfuric acid, when the gray brown amorphous mass was washed with water till the acid reaction disappeared from the wash waters. The product was then dried and treated with hot toluene. This separated it into two compounds, a purple and a yellow substance.

I. *Dianilinoquinone.*—The part almost insoluble in hot toluene was expected to be dianilinoquinone, after our experience with the dibromodiiodoquinone, so it was dissolved in hot nitrobenzene and filtered with suction. We obtained partly on the filter and partly in the filtrate the familiar purple plates of dianilinoquinone. The substance on the filter seemed a little brighter, so it was washed well with alcohol, dried, and analyzed for nitrogen.

Calculated for $C_{12}H_8(NHC_6H_5)_2O_2$: N, 9.65. Found: 9.91.

It gave with sulfuric acid the same red purple color shown by a known sample.

II. *The Yellow Compound.*—This was crystallized from boiling alcohol, each time a very small amount of a brownish substance, insoluble in cold alcohol, being left undissolved, although all the material present had been in clear solution in the alcoholic filtrate just before cooling. After several crystallizations, it was dried and analyzed.



This analysis showed that by using undiluted aniline on the diphenoxy compound, instead of the toluene solution used in the case of the dibromodiiodoquinone, a monoanil had been formed instead of the expected monoiododianilinoquinone. As the time at our disposal did not allow of the manufacture of another sample for a determination of carbon and

hydrogen, the following experiment was performed as a check. A little of the substance was boiled about three minutes with dilute hydrochloric acid, as this reagent has no effect on anilino groups, but decomposes anils, setting free aniline. The solution was filtered, and from the filtrate was obtained the isonitrile reaction, which was regarded as proof of the presence of aniline, and hence of an anil grouping in the original substance. In this connection also is to be noted the formation of an insoluble substance in small amount on each boiling of the compound with alcohol. This was presumably due to the splitting off of the anil grouping by boiling with alcohol, giving the moniododianilinoquinone, which would probably be insoluble in cold alcohol, as was the corresponding bromine derivative.

The moniododianilinoquinonemonoanil crystallizes from alcohol in fine dark needles, a deep yellow brown, usually grouped in clusters. It decomposes at about 225° , with fumes of iodine, and the resulting residue is not melted at 300° . Readily soluble in chloroform or hot alcohol, only slightly in acetone or cold alcohol, almost insoluble in ether or ligroin. It gives a full purple with strong sulfuric acid.

The Action of Cold Iodides on the Tetrahalogen Quinones.

Chloranil and Potassium Iodide.—To a saturated solution of pure chloranil in dry cold acetone was added solid potassium iodide in the form of good sized crystals, when the green precipitate appeared immediately, accompanied by the color of free iodine, the presence of which was readily shown by the starch test. After a short time the solution was gently shaken, and the liquid with the light precipitate suspended was poured off upon a Büchner funnel, when, after washing with more acetone and allowing it to dry, it was found to be grass green, and under the microscope it showed needles. It was realized that the addition of solid potassium iodide was undesirable, but it was considered unavoidable, as mixing the saturated solutions gave only a minimum precipitate, and the analyses show that by the method of floating the light precipitate away from the heavy potassium iodide, a clean separation is really effected. The precipitate was dried *in vacuo*.

Calculated for $C_6Cl_4O_2 \cdot C_6Cl_4(OK)_2$: Cl, 49.74; K, 13.74.

Found:

Cl, 49.36; K, 13.62.

The salt forms grass green needles, which dissolve in acetone to a brownish solution; it is slightly soluble in ethyl acetate, benzene, or toluene. On heating, it does not melt, but gives off a yellow sublimate, probably chloranil, and leaves a black residue. It dissolves in dilute caustic potash to form a green solution, which decomposes on warming. Pure water hydrolyzes the compound fairly rapidly, and when allowed to stand with it a long while, it gradually becomes converted into a white amorphous compound, containing no potassium. This was filtered, washed

and dried. Two different specimens were analyzed for chlorine, giving numbers close to the theory for a hemiether, but no further work was done on this substance.

Calculated for $C_6Cl_4(OH)-o-C_6Cl_4O_2$: Cl, 54.29. Found: 54.10, 54.48.

Chloranil and Sodium Iodide.—This iodide, being readily soluble in acetone, gives the green salt readily on mixing saturated solutions of the two compounds. Care was necessary that the acetone solutions should be dry and distinctly cold to the touch. The copious precipitate was filtered with suction, washed with acetone, and dried *in vacuo* for analysis.

Calculated for $C_6Cl_4O_2.C_6Cl_4(ONa)_2$: Na, 8.43. Found: 8.57.

The salt is blue green. Otherwise it corresponds in properties to the potassium compound. Dilute sulfuric acid gave a whitish precipitate, which was extracted with alcohol. From the alcohol were obtained long needles, melting at $231-233^\circ$, without recrystallization, therefore, tetrachlorohydroquinone, the melting point of which is 234° . It was readily oxidized by nitric acid to chloranil, shown by crystallization from acetone in the characteristic lemon yellow plates, which sublimed without decomposition, and melted in a closed tube at $280-282^\circ$, chloranil melting under those conditions at 290° . There were also obtained from the portion insoluble in the alcohol, by crystallization from acetone, crystals of chloranil, melting at $285-286^\circ$. Sulfuric acid, therefore, decomposes the salt into a mixture of chloranil and tetrachlorohydroquinone.

Tetrabromo-o-quinone and Sodium Iodide.—Two grams of the quinone dissolved in 15 cc. of dry acetone and 2 grams of sodium iodide dissolved in 30 cc. were mixed together, after filtering, by pouring the quinone solution into the iodide solution. The flask was then rinsed into the iodide solution with 10 cc. more of dry acetone, and the mixture shaken vigorously. The reaction was instantaneous, and the precipitate, black while wet, was filtered off with suction, washed well with acetone and finally with ether, as preliminary experiments had shown that acetone reacted with the salt on long standing. It was then well pressed out and placed in a vacuum desiccator over night. In the morning the corners of the mass had become very slightly tarry, so they were cut off, and the rest of the green salt, which was unaltered, was brought to constant weight over calcium chloride for analysis.

Calculated for $C_6Br_4O_2.C_6Br_4(ONa)_2$:

Br, 71.57; Na, 5.16.

Calculated for $C_6Br_4O_2.C_6Br_4(ONa)_2 \cdot \frac{1}{2}CH_3COCH_3$: Br, 69.32; Na, 4.99.

Found:

Br, 68.95; Na, 5.00.

The salt precipitates in bluish green needles, about the color of the salt from chloranil. It is much less stable than the other salts analyzed, decomposing on heating to 80° for a short while, probably on account of the presence of the acetone.

Like precipitates were readily obtained from bromanil and tetrachloro-*o*-quinone.

Estimation of Iodine Set Free.—For the purpose of determining the amount of free iodine formed in the reaction of iodides with bromanil, 10 grams of the powdered crystals, melting at 292–293°, were boiled two hours with 10 grams of potassium iodide in alcohol. The solution was then filtered, the precipitate washed with alcohol till no more iodine color was visible in the alcohol used for washing, and the alcohol filtrate and washings made up to 250 cc. This solution was then titrated for iodine with a thiosulfate solution, 1 cc. of which was equivalent to 0.01 gram of iodine. Much difficulty was found in estimating the end-point, as the reduction products of the quinones present darkened the liquid considerably, and obscured the blue color, so it seemed best to use but 10–15 cc. and titrate rapidly. In nine titrations, the following values were found for 1 cc. of the thiosulfate solution in terms of the iodine solution: 2.20, 2.23, 2.19, 1.19, 1.88, 2.17, 2.29, 2.34, 2.36. The average of these is 2.16, which corresponds to 1.1 grams of free iodine in solution as reaction product. The insoluble quinones from the reaction weighed 9.6 grams and melted at 253–258°. Calculated as dibromodiiodoquinone, it is equivalent to 7.9 grams bromanil, but as a matter of fact it is equivalent to less bromanil, as it was not all dibromodiiodoquinone. This corresponds roughly, then, to the disappearance as various reduction products of 2.1 grams bromanil. The 1.1 grams of iodine formed would be set free by 2.0 grams of bromanil, showing that the iodine formed, as was to be expected, really does come from reduction of the bromanil which does not appear as iodo derivative.

Potassium Iodide in Cold Alcohol on Bromanil.—Ten grams of pure bromanil, 10 grams potassium iodide and 100 cc. of alcohol were placed in an Erlenmeyer flask, closed with a rubber stopper, and allowed to stand with no heating, and with only occasional shaking, for four months. No green salt was visible at any time. The final substance in the flask was red brown; isolated as usual, it melted at 242–245°, and on crystallization from ethyl acetate, showed that the effect had been in no wise different from that produced when heated.

THE AMYGDALINS AND THEIR INTER-REACTIONS WITH EMULSIN.

BY VERNON K. KRIEBLE.

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In a previous communication¹ from this laboratory, it was proved that the rotation of a racemized amygdalin solution is independent of the nature and of the concentration of the alkali and that the equilibrium point is independent of the temperature and of the concentration of the

¹ Walker and Kriebel, *J. Chem. Soc.*, 95, 1437.

amygdalin. It was pointed out that racemic amygdalin could be partially resolved into its optical isomers. *l*-Amygdalin or ordinary amygdalin was obtained pure from the racemic by recrystallization from aqueous alcohol and afterwards from water. A part of the more soluble portion containing the dextro form was obtained with alcohol of crystallization at low temperature in absolute alcohol. The actual rotation of these anhydrous crystals did not agree with the calculated rotation of a solution made up of *d*- and *l*-amygdalin in proportion to the *d*- and *l*-mandelic acid obtained when the crystals were hydrolyzed with acid. It had also been noted that the amounts of glucose liberated by emulsin from *l*- and *r*-amygdalin was 4 : 3, which suggested that emulsin did not split off the second molecule of glucose from the dextro compound and should, therefore, have formed *d*-mandelonitrile glucoside or sambunigrin, though this substance could not be extracted. It was not sambunigrin, however, as it was not broken up by emulsin into benzaldehyde, glucose and hydrocyanic acid. It was also noted that a racemic solution dried on a water-bath for some hours had an increase in the specific rotation and that such solutions could not be hydrolyzed by emulsin to the same extent as the unheated racemic modification. These last two facts indicated that a more complicated transformation than the simple racemization was taking place and it was suggested that probably the change was from an α - to a β -glucoside.

In the present communication it is shown that the minutest trace of hydroxyl ion is capable of racemizing amygdalin and that the cyanide radicle is necessary to effect this change. The composition of the racemic amygdalin is definitely proved and shown to be made up of 56.25% of dextro and 43.75% of the levo form. The cause of the increase in rotation when racemic solutions are dried on the water bath is found to be due to a very slight amount of hydroxyl ion coming from the hydrolysis of the barium salt from an unknown acid always associated with amygdalin in minute quantities. The nature of the change giving rise to the increased rotation is conclusively proved to be a transformation of the CN radicle. When the cause was known it could easily be eliminated, after which it was possible to isolate dextro amygdalin in a pure form. Its properties are very similar to that of the levo compound, as was expected.

A very interesting fact was brought to light in connection with the hydrolysis of the amygdalin with emulsin. It had been pointed out by other investigators that emulsin not only hydrolyzes but also synthesizes active benzaldehydecyanhydrin from hydrocyanic acid and benzaldehyde. The curious part is, however, that Feist, Rosenthaler and Auld always found *d*-benzaldehydecyanhydrin in their hydrolytic solutions while we invariably obtained the levo modification in the case of certain samples of emulsin. With benzaldehyde and hydrocyanic acid

the dextro antipode is produced, which agrees with the results of the above investigators.

Experimental.

The experimental results will be taken up under the following headings:

1. The effect of the strength of alkalies upon the equilibrium between the levo and dextro amygdalin. 2. Composition of the racemic amygdalin. 3. Cyanide radicle necessary for racemization. 4. Cause of the increase in rotation of the racemic amygdalin when it is dried on a water-bath. 5. Nature of change described above as due to hydroxyl ion. 6. Resolution of racemic amygdalin: (a) Isolation of the levo form; (b) isolation of the dextro form. 7. Hydrolysis of the *d*-amygdalin by strong sulfuric acid. 8. Hydrolysis of the *d*-amygdalin by strong hydrochloric acid. 9. Action of emulsin on the amygdalin. 10. Synthesis by emulsin of *d*-benzaldehydecyanhydrin from hydrocyanic acid and benzaldehyde.

1. The Effect of the Strength of Alkalies upon the Equilibrium between Levo and the Dextro Amygdalin.

Walker¹ showed that when ordinary amygdalin is treated with dilute alkali it is rapidly changed into a substance which is much more soluble and which yields a slight preponderance of *d*-mandelic acid when hydrolyzed. During the course of the investigation it was found that this change is brought about by extremely minute quantities of hydroxyl ions, as the following experiments will show.

Amygdalin is never entirely neutral, even though it has been recrystallized five or six times. In this particular lot, 10 grams required more than 1 drop 0.25 *N* alkali, but less than 2 drops to give a pink color with phenolphthalein. When 1 drop is diluted with 25 cc. of water, it can be added to 10 grams of amygdalin, also dissolved in water to which a drop of phenolphthalein has been added, without bringing out the pink color. When this solution is boiled down a thick syrup is left instead of crystals; if it is redissolved in water and made up to 100 cc. it has the following rotation: $c = 6.944$, $t = 24^\circ$, $l = 2$ dcm., $\alpha = -9.57^\circ$, hence $[\alpha]_D^{24} -53.5^\circ$. Now 1 cc. of 0.25 *N* alkali solution contains 0.00425 gram of OH ion and, assuming that there are 20 drops in 1 cc., we would have used 0.000225 gram to racemize 10 grams, or 2 in 100,000, provided the barium salt of the acid present is completely hydrolyzed. In another experiment, 10 cc. of a 10% solution was made up to 25 cc. with a solution of barium carbonate in carbonic acid. After standing for 2 hours it still had a specific rotation of -38.4° at 23° . The solution was then immersed in boiling water for upwards of twenty minutes. Its specific rotation had changed to -48.9° , which showed that it was partly racemized. When this solution was boiled to dryness and then hydrolyzed with hydrochloric acid, it gave mandelic acid with a specific rotation of $+5.5^\circ$ (racemic gives $+18^\circ$). Here, too, the barium salt

¹ *J. Chem. Soc.*, 83, 478 (1903).

of the acid present is formed and no doubt this is hydrolyzed and gives rise to hydroxyl ions.

It is hard, however, to explain the two following experiments in this way. One cc. 0.25 *N* barium hydroxide was just neutralized with sulfuric acid, then boiled to dryness. Ten cc. of a 10% solution were added to the barium sulfate and boiled to dryness again. The syrup left was made up to 25 cc. and examined in the polariscope, $\alpha = -3.18^\circ$, $c = 3.5776$, $t = 23^\circ$, $l = 2$ dcm., hence $[\alpha]_D^{23} -44.4^\circ$. In another experiment the same quantity of barium hydroxide was neutralized with sulfuric acid until the pink color of phenolphthalein disappeared, then 10 cc. of *l*-amygdalin added and the solution boiled to dryness. When it was made up to 25 cc. and examined in the polariscope, $\alpha = -3.90^\circ$, $t = 24^\circ$, $l = 2$ dcm., hence $[\alpha]_D^{24} -54.5^\circ$. So barium sulfate freshly precipitated seems to racemize faster than when it has once become perfectly dry. This difference might be due to occluded barium hydroxide in the barium sulfate crystals, which later diffused and affected the change in rotation or to the fact that the first solution is saturated with barium sulfate and the second is not.

2. Composition of the Racemic Amygdalin.

Walker, who first discovered the racemic amygdalin,¹ pointed out that when it was completely hydrolyzed with hydrochloric acid, the ethereal extract always showed an excess of *d*-mandelic acid, indicating the production of excess of *d*-amygdalin. This has been confirmed by Dakin² and by a number of our own observations. Since the equilibrium could not be shifted and since the amygdalinic acid gives inactive acid, it was held that the racemic was an equal mixture of *l*- and *d*-amygdalin.³ The reason given for the production of excess of *d*-mandelic acid was the inequality in the rates of hydrolysis of the two varieties by acid, accompanied by a slow racemization. This is not borne out by experiment. Five grams of *l*-amygdalin (3 H₂O) were hydrolyzed with hydrochloric (D 1.118) at 60° to 70°, for 5 hours, extracted with ether 4 times and the residue from the ether made up to 50 cc. and examined in the polariscope, $\alpha = -8.44^\circ$, $l = 2$ dcm., $t = 25^\circ$, and 20 cc. needed 29.2 cc. of 0.125 *N* alkali, or $c = 2.775$; hence $[\alpha]_D^{25} -152^\circ$. So there is no racemization during the hydrolysis of the levo form, and the same is true of the dextro form from results which appear later on. As proof that the continued boiling did not racemize the mandelic acid, 1 gram was dissolved in hydrochloric acid (D 1.118) and made up to 50 cc. This rotated polarized light -3.30° in a 1 dcm. tube. The solution was heated for 10 hours, then cooled and examined

¹ *J. Chem. Soc.*, 83, 472 (1903).

² *Ibid.*, 85, 1512 (1904).

³ Walker and Krieble, *Ibid.*, 95, 1437 (1909).

again; it now had an angle of -3.28° at the same temperature. So the excess of *d*-mandelic acid must represent a corresponding excess of *d*-amygdalin in the racemic. Several grams were racemized and then hydrolyzed with hydrochloric acid (D. 1.118) for 6 hours at 60° – 70° and the acid solution extracted with ether. The ether residue was made up to 50 cc. and examined in the polariscope. $\alpha = +0.85^\circ$, $t = 25^\circ$, $l = 2$ dcm., 20 cc. needed 25.45 cc. 0.125 *N* alkali to neutralize it, but 1.65 cc. was hydrochloric acid, so $c = 2.2610$; hence $[\alpha]_D^{25} + 18.8^\circ$. At this temperature mandelic acid has a specific rotation of 150° , so the % excess of dextro in the above solution is $18.8/150 \times 100$, or 12.75. The racemic is therefore composed of 56.25% *d*-amygdalin and 43.75 *l*-amygdalin. Near the close of this investigation, the *d*-amygdalin was isolated and found to have a specific rotation of -61.2° at 19° for a 5% solution. A *l*-amygdalin solution under the same conditions has a rotation of -39.2° . If we calculate what the specific rotation of a solution ought to be if it was made up of 56.25 parts of dextro and 43.75 of levo from the above rotations we find it to be -51.6° , while the observed rotation is 52.2° for the same temperature. This is conclusive proof that the racemic is not made up of equal parts of levo and dextro amygdalin.

3. The Cyanide Radicle Necessary for Racemization.

No one has as yet suggested a theory to explain the racemization but it can be demonstrated by the following experiment that it is not possible to racemize the asymmetric carbon atom in the mandelic acid radicle—the one racemized when amygdalin is treated with alkali—unless the cyanide group is attached to it; by treating a metallic salt of active amygdalinic acid with alkali. To do this, it was necessary to prepare active amygdalinic acid. Fifty grams of *l*-amygdalin ($3 \text{ H}_2\text{O}$) were dissolved in 450 cc. of 0.25 *N* barium hydroxide and the solution boiled to expel all the ammonia. The barium was precipitated with sulfuric acid and the solution allowed to settle. The clear liquid was siphoned off into a 1 liter measuring flask, the barium sulfate carefully washed and the washings also run into the measuring flask. It was filled up to the mark and a rotation taken: $\alpha = -5.44^\circ$, $t = 21.5^\circ$, $l = 2$ dcm.; hence $[\alpha]_D^{21.5} - 60.8^\circ$ for anhydrous amygdalinic acid. To 500 cc., 8.2 grams of strychnine were added, which is the theoretical quantity necessary to produce the acid salt. This dissolved readily on boiling. The strychnine salt did not crystallize on cooling, however, so the solution was concentrated in a number of stages and then allowed to stand for some time, but there was no sign of crystallization. So another lot of 8.2 grams of strychnine was added and dissolved by boiling. When this solution was concentrated to about 100 cc. and allowed to stand for one week, very thin, long, transparent, needle-shaped crystals came down. When filtered from the mother liquor and exposed to the air they became opaque and finally

crumbled to powder, showing that they contained water of crystallization. When dried to constant weight, they weighed 18 grams. A 1% solution had a specific rotation of $[\alpha]_D -26.5^\circ$. One and two-tenths grams dissolved in water required 11 cc. of 0.125 *N* alkali to neutralize the acid. Amygdalinic acid ($C_{19}H_{27}O_{11}COOH$) has a molecular weight of 476; therefore, 11 cc. of 0.125 *N* solution would represent 0.6545 gram. Strychnine ($C_{21}H_{22}N_2O_2$) has a molecular weight of 334, so for every 476 parts of amygdalinic acid there would be 334 of strychnine or 0.6545 gram of amygdalinic acid would be combined with 0.4592 gram of strychnine. It is evident, therefore, that the 1.2 grams of the strychnine salt contained 0.0863 gram of water, which corresponds to $3\frac{1}{2}$ molecules of water of crystallization. This was verified by drying a portion over phosphorus pentoxide in a tube exhausted to 50–70 mm. and heated to 90° . 0.83 gram of the salt lost 0.0612 gram H_2O , corresponding to $3\frac{1}{2}$ molecules.

To show that optically active amygdalinic acid cannot be racemized, 5 grams of crystallin strychnine amygdalinate were dissolved in water and 1 cc. more 0.25 *N* barium hydroxide added than was necessary to precipitate the strychnine. After one hour the alkali was neutralized and the solution made up to 50 cc. The specific rotation of the barium salt was $c = 4.605$, $\alpha = -3^\circ$, $t = 21.5^\circ$, $l = 2$ dcm., hence $[\alpha]_D^{21.5} -32.5^\circ$. The solution was filtered and concentrated to a thick syrup, then hydrolyzed with hydrochloric acid. The extracted mandelic acid was made up to 50 cc. and examined in the polariscope. It had an angle of $+2.75^\circ$ in a 2 dcm. tube at 22° ; its concentration was 1.7765 grams; hence $[\alpha]_D^{22} +77.4^\circ$. The excess of dextro in the crystals is, therefore, $77.4/149 \times 100$, or 52%, which shows that the amygdalin radicle cannot be racemized if the cyanide group is absent.

As active mandelonitrile was obtained near the end of this investigation it was found that the asymmetric carbon atom present could be racemized if the nitrile was dissolved in ether and a few drops of dilute alkali added.

4. Cause of the Increase in Rotation of the Racemic Amygdalin.

As already pointed out in the introduction, we were considerably baffled by the behavior of the racemic amygdalin. We always had a large portion which could not be obtained crystallized. Emulsin did not seem to hydrolyze the racemic forms completely and the end-point of the hydrolysis seemed to be influenced by the length of time the racemic compound was dried on the water bath. It took a long time, however, to find out what caused this change. At first it was thought to be due to the presence of barium carbonate, which slightly dissolves in the racemic solution when saturated with carbon dioxide. So oxalic and sulfuric acids were used to neutralize the barium hydroxide but in almost every case the rotation increased, as the following table shows.

A 10% stock solution of *l*-amygdalin ($3 \text{ H}_2\text{O}$) was made up. Ten cc. were used in each experiment, to which was added 1 cc. of 0.25 *N* barium hydroxide and then treated as follows:

(1) Passed in carbon dioxide until neutral to phenolphthalein, filtered and boiled for five hours on water-bath. Made up to 25 cc. and examined in the polariscope.

$$\alpha = -4.60^\circ, t = 24^\circ, l = 2 \text{ dcm.}, \text{ hence } [\alpha]_D^{24} -64.3^\circ.$$

(2) Passed in carbon dioxide until saturated, then boiled ten minutes before filtering. Filtrate was boiled for 5 hours.

$$\alpha = -4.70^\circ, t = 24^\circ, l = 2 \text{ dcm.}, \text{ hence } [\alpha]_D^{24} -65.7^\circ.$$

(3) Added oxalic acid until neutral to phenolphthalein. Evaporated and heated 5 hours.

$$\alpha = -4.60^\circ, t = 25^\circ, l = 2 \text{ dcm.}, \text{ hence } [\alpha]_D^{25} -64.3^\circ.$$

(4) Added sulfuric acid until neutral to phenolphthalein, then evaporated and boiled 5 hours.

$$\alpha = -4.56^\circ, t = 23^\circ, l = 2 \text{ dcm.}, \text{ hence } [\alpha]_D^{23} -63.7^\circ.$$

(5) (12.5 cc. used instead of 10 cc.) Neutralized with theoretical quantity of oxalic acid, evaporated and heated for $5\frac{1}{2}$ hours then made up to 25 cc.

$$\alpha = -4.70^\circ, t = 20^\circ, l = 2 \text{ dcm.}, \text{ hence } [\alpha]_D^{20} -52.5^\circ.$$

These are only a few selected at random from the notebook. There were very few where the rotation did not increase. Finally, it was noticed that all the solutions which had an increased rotation gave a faint precipitate with sulfuric acid, while solutions heated like number 5 did not give a precipitate. This gave a clue to the situation, as it suggested that the amygdalin solutions were faintly acid and that when the barium hydroxide was added this acid was changed to the barium salt. When the excess of barium hydroxide was neutralized, this barium would not be precipitated, as there was just enough added to make the solution neutral to phenolphthalein. To show that this was actually the case, 1 drop of barium hydroxide was added to 10 grams of *l*-amygdalin ($3 \text{ H}_2\text{O}$) in solution, but as I have already said, this did not change the phenolphthalein red. When the solution was evaporated to a syrup and then made up to 100 cc., it had a specific rotation of $c = 8.944$, $\alpha = -9.57^\circ$, $l = 2 \text{ dcm.}$, $t = 24^\circ$; hence $[\alpha]_D^{24} -53.5^\circ$. Ten cc. of this solution were evaporated to dryness and heated for 5 hours, then made up to 25 cc. It now had a rotation of $c = 3.5776$, $\alpha = -4.70^\circ$, $l = 2 \text{ dcm.}$, $t = 24^\circ$; hence $[\alpha]_D^{24} -65.7^\circ$. This was repeated with the same result.

To prove that this change must be due to the hydroxyl ions caused by the hydrolysis of the barium salt, 1 drop of *N* sulfuric acid was added to 10 cc. of the above 100 cc. and heated for 5 hours and then made up to 25 cc. again. It had a rotation of $c = 3.5776$, $\alpha = -3.75^\circ$, $t = 24^\circ$, $l = 2 \text{ dcm.}$; hence $[\alpha]_D^{24} -52.4^\circ$. This was repeated with a 10-gram lot to which 5 cc. excess oxalic acid (0.33 *N*) were added when the barium hydroxide was neutralized, with the same result. A very small amount of hydroxyl ions, therefore, does not only racemize, but also appears

to change the amygdalin in some way, when present during the evaporation of the solution.

5. Nature of the Change Caused by Hydroxyl Ions in Racemic Solutions when Evaporated to Dryness and Baked on Water Bath.

The most natural thing to expect when the specific rotation went up was that there was more of the dextro form produced. Six grams were, therefore, dissolved in water and added to a solution of 100 cc. containing 2 cc. of barium hydroxide, which had been precipitated and redissolved by passing in carbon dioxide. The solution was taken down to a very thick syrup. This was afterwards made up to 50 cc. and a rotation taken: $\alpha = -12.44^\circ$, $l = 2$ dcm., $t = 23^\circ$, $c = 10.7328$; hence $[\alpha]_D^{23} -58^\circ$. The solution was evaporated to a thick syrup and hydrolyzed with hydrochloric acid (D 1.118) for 4 hours at 60° – 70° , the mandelic acid extracted and made up to 50 cc. It had a dextro rotation of 0.20° in a 1 dcm. tube at 22° , 20 cc. used up 38.1 cc. 0.125 *N* alkali or $c = 3.6195$; hence $[\alpha]_D^{22} +5.5^\circ$. This shows that the equilibrium has not been shifted in favor of the dextro form.

Since barium could always be precipitated from solutions which had this high rotation and racemic solutions whose rotation did not go up did not contain barium, it was conceivable that the barium was in some way united with the glucose part of the molecule which caused this increase in rotation. One gram of *l*-amygdalin ($3 \text{ H}_2\text{O}$) was, therefore, dissolved in water, $\frac{1}{2}$ cc. of barium hydroxide added, and then oxalic acid added until the color of the phenolphthalein had just disappeared. The solution was evaporated to dryness and baked on the water-bath for 5 hours. It was then made up to 50 cc. and had the following rotation: $\alpha = -4.55^\circ$, $t = 25^\circ$, $l = 2$ dcm., $c = 3.5776$; hence $[\alpha]_D^{25} -63.9^\circ$. Twenty-five cc. of this solution were treated with dilute sulfuric acid until it no longer gave a precipitate, and then evaporated to 25 cc. and another rotation taken. It now rotated polarized light -4.40° at 23° in a 2 dcm. tube, or $[\alpha]_D^{23} -63^\circ$, which shows that the combination of barium with the glucose radicle is not the cause of the increase in rotation.

If the cause of this high rotation exists in the glucose part of the molecule, then the corresponding ammonium amygdalinate ought also to have an increased rotation. So 2.5 grams *l*-amygdalin ($3 \text{ H}_2\text{O}$) were boiled with excess of barium hydroxide until all the ammonia was expelled, then ammonia and carbon dioxide were passed in to precipitate all the barium. The solution was filtered, the precipitate carefully washed and the clear filtrate evaporated to 50 cc. It had a specific rotation of $\alpha = -6.47^\circ$, $l = 2$ dcm., $t = 19^\circ$, $c = 4.472$; hence $[\alpha]_D^{19} -72.3^\circ$. This was repeated some time later when $[\alpha]_D^{24}$ was found to be -71.8° . When the ammonium amygdalinate was prepared from the racemic form which had the increased rotation, it was found, however, to be the same. Two

and five-tenths grams of *l*-amygdalin ($3 \text{ H}_2\text{O}$) were dissolved in water, 2 cc. barium hydroxide added and after 10 minutes carbon dioxide passed in. The solution was evaporated to dryness and baked for 7 hours, then made up to 50 cc. The specific rotation was $c = 4.472$, $\alpha = -5.43^\circ$, $l = 2 \text{ dcm.}$, $t = 24.5^\circ$; hence $[\alpha]_D^{24.5} = -60.7^\circ$. Twenty-five cc. of the solution were changed to ammonium amygdalinate by the method described above. When it was made up to 25 cc., it had a specific rotation of $[\alpha]_D^{23} = -71.6^\circ$. This shows that the change of rotation in the racemic form when heated is not due to any change in the glucose part of the molecule or else the corresponding ammonium amygdalinate would not have the same rotation. As further proof, ammonium amygdalinate was heated for 7 hours in the presence of a small quantity of freshly precipitated barium carbonate, but when redissolved it was found to have the same rotation.

From these results one would suspect that the cyanide group was changed or hydrolyzed in some way. This could easily be proved as it was pointed out¹ that strong sulfuric acid when allowed to act on *l*-amygdalin for several hours at a high temperature, produced about 85% of the theoretical *d*-mandelonitrile, so if the cyanide has been hydrolyzed during the change that takes place when the rotation of the racemic form goes up, it ought not to give any nitrile when hydrolyzed with strong sulfuric acid. Twenty grams of the racemic amygdalin were, therefore, heated with a small quantity of barium carbonate for 6 hours when the specific rotation went up to -67.4° . The solution was again evaporated and the thick syrup dissolved in 60 cc. of water and 40 cc. of concentrated sulfuric acid. This solution was heated to 90° and kept at this temperature for $1\frac{1}{2}$ hours, after which it was cooled and extracted with 100 cc. of benzene. The benzene solution did not have any activity. It was evaporated to a small volume, then poured into a small beaker and when free of the solvent and moisture it weighed 0.287 gram, which is only an eighth of the nitrile obtained from *l*-amygdalin. The aqueous hydrolytic solution was extracted with ether and the mandelic acid obtained was dissolved and made up to 100 cc. with water. It had a slight dextro activity. Ten cc. required 26.6 cc. of 0.125 *N* alkali or the concentration of mandelic acid was 5.12 grams. This demonstrates that the nitrile was hydrolyzed before the sulfuric acid acted, because when *l*-amygdalin is treated for the same length of time with the same strength of acid it yields about 85% of nitrile while in this case 86% of mandelic acid was obtained.

It is difficult to say to what the nitrile radicle is transformed when the racemic amygdalin is heated, as it is impossible to get the new substance pure. One might expect it to be ammonium amygdalinate from its rotation. There are no ordinary tests, however, which can be applied

¹ Walker and Krieble, *J. Chem. Soc.*, 95, 1369 (1909).

in this case, so the electrical resistance of this substance was compared with that of ammonium amygdalinate. The cell used had a constant of 0.1037 and a 5% *l*-amygdalin (3 H₂O) solution had a conductivity of 0.424×10^{-4} . Ammonium amygdalinate was prepared according to methods already described.

The following are some of the conductivities observed, measurements being made at 25°.

Per cent of NH ₄ amygdalinate.	Specific rotation.	Specific conductivity.
5	—71.8°	6.74×10^{-8}
4	..	5.18×10^{-8}
3 $\frac{1}{2}$..	4.45×10^{-8}
2	..	3.45×10^{-8}
3% of NH ₄ amygdalinate + 1% of <i>l</i> -amygdalin	—63°	3.99×10^{-8}

The following are the solutions which had been heated:

4	—65.4°	5.94×10^{-4}
4	—58.2°	3.61×10^{-4}
4	—67.5°	5.98×10^{-4}
4	—64.6°	5.08×10^{-4}

From these results it is quite evident that this new substance is not ammonium amygdalinate nor even a mixture of amygdalin and ammonium amygdalinate. It might be the amide or some other nitrogen derivative of amygdalinic acid, but it cannot be the acid itself as it is very nearly neutral in reaction, nor can it be the barium salt, as there is only the faintest trace of barium in it. At this point our attention was turned to the isolation of the *d*-amygdalin, as we had found out how to evaporate the racemic form without bringing about any internal change.

6. Resolution of Racemic Amygdalin.

Seventy-five grams were dissolved in several hundred cc. of luke-warm water and 6 cc. of barium hydroxide added. After one-half hour, 1.4 cc. of 0.33 *N* oxalic acid were added in excess of the quantity needed to make the solution neutral. This was evaporated to a moderately thick syrup and 250 cc. of 95% alcohol added, which caused 30 grams of crystals to separate. It was impossible to get any more crystals by concentrating the mother liquor, so the alcohol was distilled off *in vacuo* and the syrup drawn out to a froth. The flask was then broken and the residue dried in a vacuum desiccator, after which it was dissolved in 500 to 600 cc. of boiling absolute alcohol. When the solution cooled to the room temperature, a small quantity (5 grams) of a heavy syrup separated. This is due to the fact of not using enough alcohol as it was not obtained in subsequent experiments. So the clear solvent was decanted and cooled to —5° for an hour, which caused 7.6 grams of a fine crystallin precipitate to separate. This was rapidly filtered and washed with cooled ab-

solute alcohol. When the temperature went up a few degrees it liquefied completely giving off its alcohol of crystallization. The mother liquor was concentrated to $\frac{1}{3}$ of its original volume and allowed to stand at the room temperature for several days. During this time 11.8 grams of crystals separated, which, so far as could be ascertained, did not contain alcohol of crystallization. The solution was again concentrated, but no more crystals separated, so it was cooled with salt and ice, which caused 4 more grams of crystals with alcohol of crystallization to separate. It was concentrated a third time, which caused another crop of 2.6 grams to come out, at room temperature. When the mother liquor was concentrated a fourth time and cooled with a freezing mixture, 3.2 grams separated. The solvent was then completely evaporated which left a residue of 3.34 grams. It is possible, therefore, to resolve the racemic amygdalin practically completely into three different mixtures all of which, however, are crystalline. The final residue of 3.34 grams was rather sticky and when tested was found to be slightly acidic in nature, which showed that prolonged boiling hydrolyzes a very small fraction.

(a) Isolation of the Levo Amygdalin.

The first crop of crystals (30 grams) contains a large preponderance of *l*-amygdalin. A 5% solution in a 2 dcm. tube at 20° rotated polarized light -4.11° . When 1.366 grams were dried over phosphorus pentoxide *in vacuo* at reduced pressure it lost 0.0928 gram or 6.8% of water of crystallization; hence $[\alpha]_D^{20} -44^\circ$. Five grams were hydrolyzed in the usual way and the mandelic acid extracted, dissolved and made up to 50 cc. It had a specific rotation of $\alpha = -6.40^\circ$, $l = 2$ dcm., $t = 24.5^\circ$ and 20 cc. required 31.4 cc. of 0.125 *N* alkali, or $c = 2.983$; hence $[\alpha]_D^{24.5} -107.3^\circ$. At this temperature mandelic acid has a rotation of -150.5° , therefore, this fraction contains about 85.6% of the levo isomer and 14.4 of the dextro. If one calculates what the rotation of such a mixture should be at 20°, it comes to -42.5° , which is not very far from the value found when one takes into consideration the number of experimental facts that the theoretical depends on. About 20 grams of the above 30 were dissolved in a small quantity of hot water. When the solution cooled, the levo compound crystallized out in rosetts. These were twice recrystallized and then air-dried. A 5% solution (3 H₂O) showed a rotation of -3.43° in a 2 dcm. tube at 25°, or $[\alpha]_D^{25} -38.3^\circ$, which agrees very well with the *l*-amygdalin we started with, namely $[\alpha]_D^{25} -38.6^\circ$ for the same concentration. Five grams of it were hydrolyzed and the mandelic acid obtained without purification, had a specific rotation of $\alpha = -65.9^\circ$, $t = 26.5^\circ$, 20 cc. required 23.7 cc. 0.125 *N* alkali, or $c = 2.2344$; hence $[\alpha]_D -152.6^\circ$ at 17°, which compares favorably with -154° , the value found for carefully purified mandelic acid. Whether this crop of crystals which has a specific rotation of -44° is a definite compound,

made up of 3 parts of levo to 1 of dextro, saturated with the mother liquor which contains a big excess of dextro; or whether it is *l*-amygdalin saturated with the mother liquor is hard to determin. The crystals themselves come out of the alcoholic solution in the form of rosets and have all the characteristics of *l*-amygdalin. Then their rotation is not constant, for if they are washed with a small quantity of alcohol it comes down as low as -42.5° . If it is a definit compound it is very loosely bound together, as there is no difficulty whatever in isolating the pure levo form from it in good quantities.

(b) Isolation of the Dextro Amygdalin.

After the greater part of the *l*-amygdalin is separated from the racemic, the *d*-amygdalin is obtained in two crystallin modifications as already stated. The second fraction (11.8 grams) has a specific rotation of $c = 4.82$, $t = 20.5^{\circ}$, $\alpha = -5.66^{\circ}$; hence $[\alpha]_D^{20.5} -59^{\circ}$. Three and five-tenths grams were hydrolyzed in the usual way with hydrochloric acid. The mandelic acid was extracted with ether, dissolved and made up to 50 cc. with water. It showed a rotation of $+6.65^{\circ}$ in a 2 dcm. tube at 18.5° , 20 cc. required 24.6 cc. 0.125 *N* alkali; c , therefore, = 2.337; hence $[\alpha]_D^{18.5} +142^{\circ}$. So this fraction is about 95% pure *d*-amygdalin. After recrystallizing this fraction twice from absolute alcohol, it had a specific rotation of $c = 6$ (anhyd.), $\alpha = -7.27^{\circ}$, $l = 2$ dcm., $t = 27^{\circ}$; hence $[\alpha]_D^{27} -60.6^{\circ}$. When hydrolyzed, as we shall see later, it yields pure *d*-mandelic acid. It melts sharply at 212° , is easily soluble in 95% alcohol, fairly insoluble in absolute alcohol and crystallizes out slowly from a supersaturated solution in very fine fluffy crystals. It dissolves in less than its own weight of water, but assumes a crystallin form when evaporated to a thick syrup and allowed to stand for a day or two. It has a bitter taste and is hydrolyzed to glucose, hydrocyanic acid and benzaldehyde by emulsin.

The following table shows that the specific rotation of the *d*-amygdalin varies with temperature and concentration, as was conjectured from the rotation of the racemic:

<i>c</i> .	α .	<i>T</i> .	<i>l</i> .	Specific rotation.
8.5	-10.62°	14	2 dcm.	-62.5°
8.5	-10.43°	24.5	2	-61.4°
8.5	-10.19°	36.5	2	-60°
4.25	-5.13°	27	2	-60.4°
2.125	-2.51°	26.5	2	-59.2°

The other modification of the dextro form, namely, the one which crystallizes with alcohol of crystallization, has a specific rotation of $c = 4.96$, $l = 2$ dcm., $t = 26^{\circ}$, $\alpha = -5.57^{\circ}$; hence $[\alpha]_D^{26} -56.1^{\circ}$. About 3 grams were hydrolyzed and the mandelic acid extracted. It was made up with water to 50 cc. and a rotation taken: $l = 2$ dcm., $t = 27^{\circ}$, $\alpha = +3.23^{\circ}$,

20 cc. required 20.16 cc. of 0.125 *N* alkali; hence $[\alpha]_D^{27} + 84.3^\circ$, which corresponds to 78.3% of dextro and 21.7% of levo amygdalin. When one calculates what the specific rotation ought to be, it comes to -56.4° at 19° which is practically the same as the one observed. This modification seems to be a definite compound composed of 3 parts dextro and 1 of levo, mixed with a small quantity of dextro. It crystallizes with alcohol of crystallization, which the dextro compound alone does not appear to do. It is much more readily soluble in absolute alcohol than the dextro form. When such a solution is cooled, a part of the dextro form crystallizes out; if it is not filtered out, however, but allowed to stand for some hours, it reunites with the portion still in the mother liquor, forming a thick syrup which can be redissolved by heating the solvent and the process repeated. At a temperature slightly higher than the room temperature this modification, therefore, seems to be unstable, allowing the dextro form to separate.

7. Hydrolysis of Dextro Amygdalin with Strong Sulfuric Acid.

As the *l*-amygdalin acted so peculiarly towards acids, it seemed worth while to hydrolyze the *d*-amygdalin and see whether it acted in the same way. Five grams of *d*-amygdalin were, therefore, hydrolyzed in a solution containing 10 grams of sulfuric acid and 15 grams of water for 1 hour and 15 minutes at 90° . Fifteen minutes after the heating was begun, the solution turned milky and very soon beads of oil began to appear. At the end of the time specified, the solution was cooled and extracted with 50 cc. of benzene. It rotated polarized light -3° in a 1 dcm. tube. The benzene solution was collected and evaporated to dryness which left a dark colored oil free from the odor of benzaldehyde. It weighed 1.235 grams or about 85% of the theoretical nitrile in 5 grams. The aqueous hydrolytic solution was extracted with ether and the mandelic acid obtained was dissolved and made up to 25 cc. It had an angle of $+2.95^\circ$ in a 2 dcm. tube at 27° , 20 cc. required 11.8 cc. of 0.125 *N* alkali, or the 25 cc. contained 0.279 gram of mandelic acid. This demonstrates that the dextro compound loses its glucose before the cyanide radicle is attacked in a strong sulfuric acid solution. This is identical with the hydrolysis of the levo form.¹

8. Hydrolysis of Dextro Amygdalin with Hydrochloric Acid (D. 1.118) at the Room Temperature.

Five grams of *d*-amygdalin were dissolved in hydrochloric acid (D. 1.118), the solution being made up to 25 cc. The hydrolysis was carried on at the room temperature and followed by taking readings in a 1 dcm. polariscope tube.

¹ *J. Chem. Soc.*, 95, 1374 (1909).

Time.	Rotation.	Time.	Rotation.
5	-11.85°	119	+10.75°
7	-7.80°	143	+12°
23	-1.20°	167	+13°
30	+0.73°	215	+15°
47	+3.95°		

I tried to take another reading 48 hours later, but the mandelic acid had already started to crystallize out. What was left of the hydrolytic solution was extracted with ether and the mandelic acid obtained was dissolved in water and the solution made up to 50 cc. It had an angle of +5.75°, $t = 27^\circ$, $l = 2$ dcm., 20 cc. required 20.7 cc. 0.125 *N* alkali, or $c = 1.966$; hence $[\alpha]_D^{27} + 147^\circ$. Since carefully purified mandelic acid has a specific rotation of +149° at this temperature, our *d*-amygdalin must have been pure. By comparing the polariscope readings with those taken in the hydrolysis of the *l*-amygdalin, we notice that there is a very sharp drop in the rotation of the former and a corresponding rise in the latter. This strengthens the view expressed by Walker¹ that the first product formed is principally amygdalinic acid, which is then hydrolyzed to glucose and mandelic acid.

9. Action of Emulsins on the Amygdalin.

Liebig and Wohler² first pointed out that amygdalin was decomposed into glucose, benzaldehyde and hydrocyanic acid by emulsin. Since then several papers have appeared on this subject by Tammann,³ Caldwell and Courtlaud,⁴ and Auld.⁵

The following are the main conclusions arrived at: First, that for small concentration of the enzyme the velocity is proportional to its concentration. As the concentration is increased this relationship ceases and finally a further increase does not produce a corresponding increase in velocity. Second, that a constant quantity and not a constant fraction of amygdalin is hydrolyzed in a unit time, at least when a large excess of amygdalin is present. Third, that amygdalin is almost completely hydrolyzed into glucose, benzaldehyde and hydrocyanic acid by emulsin. Liebig believed that the hydrolysis went on as long as the benzaldehyde dissolved in water. Tammann noted a decomposition of 60% at 40°. Caldwell and Courtlaud, repeating Tammann's experiments, find that at the end of 67 and 90 hours, 98.2 and 98.5%, respectively, is decomposed. Fourth, that mandelonitrile glucoside is first formed, which in turn breaks down to benzaldehyde and hydrocyanic acid. The first part of the hydrolysis, therefore, takes place at the biose linking just as it does with

¹ *J. Chem. Soc.*, 83, 476 (1903).

² *Ann.*, 22, 1.

³ *Z. physik. Chem.*, 16, 271 (1892).

⁴ *J. Chem. Soc.*, 91, 670 (1907).

⁵ *Ibid.*, 93, 1251 (1908).

maltose,¹ but the hydrolysis of maltose stops here, while emulsin goes one step further.

The action of emulsin on the racemic amygdalin has not been the subject of much investigation. Dakin² noted that if a solution of emulsin is added to a racemized solution of amygdalin and kept at 40° for some time, benzaldehyde and hydrocyanic acid were found present in the solution. This only shows, however, that there is still *l*-amygdalin in the solution, but proves nothing concerning the action of emulsin on the *d*-amygdalin. So a series of comparative experiments were carried out to determine this action on the various amygdalins. The emulsin used was Kahlbaum's preparation. The solution employed was made up by adding 1 gram of the emulsin to 100 cc. of water. This was stirred at intervals during several hours, after which it was filtered into a bottle and several drops of toluene added. The extent of the hydrolysis in most cases was estimated by determining the amount of hydrocyanic acid produced. At first, Auld's method³ was used, which consists of adding an excess of sodium acid carbonate and then titrating the hydrocyanic acid with dilute standard iodine solution. It was not very satisfactory, as the end was by no means sharp. A second method that was tried, was to make the hydrolytic solution alkaline with magnesium hydroxide and add several drops of potassium chromate, then titrate with silver nitrate until silver chromate is precipitated. Still another method employed was to add excess of silver nitrate to the emulsin solution then titrate the excess with ammonium thiocyanate, using ferric alum as an indicator. These methods were tested by estimating standard potassium cyanide in an emulsin solution containing benzaldehyde, but the amount of cyanide determined was always too low. Correct values could be obtained when the emulsin was left out, which seemed to indicate that the silver nitrate in some way united with the emulsin.

A new method was, therefore, devised which gave better results than any of those mentioned above. It consisted in sucking a slow current of pure air through the Erlenmeyer flask in which the hydrolysis was carried on and then through a U-tube which held a caustic soda solution. In this way most of the hydrocyanic acid was fixed as it was liberated, which prevented it from being oxidized to formic acid. The last traces of the acid were removed by boiling the hydrolytic solution at the end of the reaction. This was not boiled into the caustic soda solution, however, but into a U-tube which contained a given amount of standard silver nitrate. This was afterwards transferred to a 100 cc. measuring flask, 2 cc. of concentrated nitric acid added, and then the caustic soda

¹ Fischer, *Ber.*, 28, 1508.

² *J. Chem. Soc.*, 85, 1517 (1904).

³ *Ibid.*, 93, 1264 (1908).

solution containing the cyanide, and filled up to the mark. The silver cyanide was filtered out and the filtrate titrated with ammonium thiocyanide. The reason that the air was passed through caustic soda at first and not through silver nitrate was because the silver cyanide which precipitated clogged up the small glass tubes with which the U-tube was filled. This would stop the flow of air and consequently the result was of no use. This method was tested and found satisfactory by putting standard potassium cyanide solution into the Erlenmeyer flask and then admitting dilute sulfuric acid, the hydrocyanic acid being carried over and estimated as specified above. The Erlenmeyer flasks in which the hydrolysis was carried on were kept in a thermostat at 41° to 43° for the length of time specified.

Amount of <i>L</i> -amygdalin used. Cc.	Length of time hydrolyzed. Hours.	Number of emulsin used. Cc.	Amount of HCN produced. Gram.	Per cent decomposition.
10 of 3% sol. (3 H ₂ O)	24	10	0.01499	94.9
10% (3 H ₂ O)	24	10	0.01510	95.6
10	9	10	0.01240	78.5
10 of 3% (anhyd.)	4	10	0.00879	49.6
Racemic Amygdalin.				
10 of 3% (3 H ₂ O)	9	10	0.01085	68.9
10	24	10	0.01223	77.5
10	24	10	0.01206	76.3
10	42	10	0.01292	81.8
10	42	10	0.01269	80.3
Dextro Amygdalin.				
10 of 3% (anhydrous)	24	10	0.01607	90.7
10	24	10	0.01558	88.0
10	4	10	0.00803	45.4

It is obvious from the above results that the dextro amygdalin as well as the levo amygdalin is hydrolyzed into benzaldehyde, glucose and hydrocyanic acid, though at a slower rate. It seems hard to explain, however, why it is that the racemic form is decomposed more slowly than both the levo and the dextro separately. There were a great many more experiments carried out than the ones quoted here, but none of them showed greater decomposition. The glucose was also estimated, both at the end of 9 hours and at 24 hours. At the end of 9 hours, 1.92 grams were liberated from 3 grams of racemic amygdalin (3 H₂O), or 91%, and at the end of 24 hours, 2 grams, or 94.7%. This showed that the most of the undecomposed substance was the mandelonitrile, which was verified by the following experiment:

Fifteen grams of racemic amygdalin were made up approximately to 250 cc. with water, 1 gram of emulsin added and the flask thoroughly shaken. It was kept in the thermostat at 41° for 15 hours and then extracted twice with 150 cc. of ether each time. When the ether was

evaporated to a volume of 50 cc. it was examined in a polariscope and found to be quite inactive. The rest of the ether evaporated spontaneously leaving an oily residue which had a very strong odor of benzaldehyde. This residue was hydrolyzed with hydrochloric acid and evaporated to dryness, then extracted 3 times with ether. It left a solid, 0.776 gram, which was filtered off and dried. This was dissolved and the solution made up to 100 cc., 20 cc. were added to 35 cc. 0.1 *N* silver nitrate. It required 28.35 cc. of *N*/47 ammonium thiocyanate to titrate the excess of silver. From this titration the 100 cc. would contain 0.7768 gram of ammonium chloride, which would be the amount yielded from 1.929 grams of nitrile, or 49.4% of the total quantity in 15 grams of amygdalin.

10. Synthesis of Active Benzaldehydecyanhydrin from Benzaldehyde and Hydrocyanic Acid with Emulsin.

During the time the above experiments were being carried out there appeared a paper by Feist¹ in which it was pointed out that if emulsin was allowed to act on a solution containing amygdalin for several days and then extracted with ether, the ether was always found to be dextro rotatory. This activity was shown to be due to *d*-mandelonitrile, which Feist supposed was one of the primary decomposition products. Several months later, Rosenthaler² showed that benzaldehyde and hydrocyanic acid in the presence of emulsin formed *d*-mandelonitrile, which put Feist's supposition in doubt, because the chances are even that the active nitrile which he isolated was a synthetic product and not a decomposition product. This was followed by a paper by Auld,³ who showed that the nitrile was produced much faster from benzaldehyde and hydrocyanic acid than from an equivalent concentration of *l*-amygdalin, using the same quantity of emulsin. Auld argued, therefore, that it was exceedingly probable that the nitrile always found in emulsin hydrolytic solutions was a secondary product formed from the benzaldehyde and hydrocyanic acid and not a primary decomposition product as supposed by Feist. Feist repeated his original experiment with a new sample of emulsin and found that the activity was much less than in his first experiment. This demonstrated that not all emulsins were alike, which made us curious to see what our emulsin did, especially since the ethereal extract from the racemic amygdalin showed no activity.

Five grams of *l*-amygdalin were dissolved in 75 cc. of water and 0.5 gram emulsin added. The flask was thoroughly shaken and kept in a thermostat at 41° for 3½ hours. The emulsin was precipitated, the solution filtered and extracted with ether. The solvent was distilled to 15 cc. and examined in a polariscope tube, but it was found to be inactive.

¹ *Arch. Pharm.*, 246, 206-9 (1908).

² *Ibid.*, 246, 365-6 (1908).

³ *J. Chem. Soc.*, 95, 927 (1909).

Since this was inactive, Rosenthaler's experiment was tried. Four-tenths gram of emulsin was dissolved in 25 cc. of water to which was added 20 cc. of 1.62% hydrocyanic acid and 2 cc. of benzaldehyde. This solution was kept at 25° for 3½ hours, then filtered through a filter covered with freshly precipitated alumina and the filtrate extracted with 20 cc. of ether. In the first two experiments there was no activity noticed in this ethereal solution, but the third had a dextro rotation of 0.15° in a 2 dcm. tube. This is very small, however, as Rosenthaler, with the same conditions, got an activity of over a degree. Consequently this sample of emulsin contains very little of the synthetic enzyme. As there was another unopened sample of Kahlbaum's emulsin in the laboratory, this was also tried. In an experiment carried out identically to the one above the ether extract when examined in a 2 dcm. tube had a dextro rotation of 0.95°. This was repeated and the second time the activity in a 2 dcm. tube was 0.98°. This time the ether was completely evaporated and the nitrile which was left was hydrolyzed with hydrochloric acid. The mandelic acid was not extracted, but the hydrolytic solution itself (50 cc.) was examined in the polariscope. In a 2 dcm. tube its activity was -1.80°. This confirmed Feist's results that emulsin does not always contain the same quantity of the synthetic enzyme.

l-Amygdalin was also hydrolyzed with this emulsin to see if more active nitrile could be obtained than with the old emulsin. Five grams of *l*-amygdalin were dissolved in 75 cc. of water and 1 gram of the new emulsin added. It was kept at 40° for 3½ hours, then extracted with 20 cc. of ether. This had a levo activity of 0.17° in a 2 dcm. tube. In the second experiment only ½ gram of emulsin was used. The activity this time was -0.15°. The third time the hydrolysis was allowed to go on for 24 hours instead of 3½, and this time the activity was only -0.12°. The ether solutions from the three experiments were poured together, the solvent evaporated and the residue hydrolyzed with hydrochloric acid. The mandelic acid was extracted and dissolved in enough water to make 25 cc. This solution had an angle of +0.6° in a 2 dcm. tube. This is a surprising result as Feist, Rosenthaler, and Auld always got a dextro nitrile yielding levo mandelic acid upon hydrolysis. To make perfectly sure that our nitrile was actually levo, the experiment was repeated using 10 grams of *l*-amygdalin and 1 gram of emulsin. But the ether solution again had an activity of -0.10°, and when the nitrile was hydrolyzed and the mandelic acid made up to 25 cc., it had a dextro rotation of 0.35°. Here then we have an example where emulsin produces a dextro mandelonitrile from commercial benzaldehyde and hydrocyanic acid and a levo nitrile when these two chemical compounds are obtained from *l*-amygdalin, because we cannot argue that the levo nitrile obtained in the second case is a primary decomposition product since the *l*-amyg-

dalín contains dextro mandelonitrile. This looks as though there might be two different benzaldehydes but this assumption could not be proved definitely. As the first sample of emulsin produced very little active nitrile, it was used to hydrolyze *l*-amygdalin and the benzaldehyde obtained was used instead of the commercial in a synthetic experiment. The experiment was carried out in the following manner: Ten grams of *l*-amygdalin and 1 gram emulsin (old) were dissolved in 150 cc. water and kept at 40° for 3½ hours. The enzyme was precipitated with a drop of acetic acid and filtered out. The filtrate was extracted with ether and the solvent evaporated. To 2 cc. of this residue ½ gram of emulsin, dissolved in 20 cc. water, was added and 25 cc. of the hydrocyanic solution (1.62%). This solution was kept at 25° for 3½ hours, when the emulsin was again precipitated and the clear filtrate extracted with ether. The residue after the solvent was evaporated was hydrolyzed with hydrochloric acid. The hydrolytic solution (25 cc.) had an angle of -0.90° in a 2 dcm. tube, showing that dextro nitrile was produced. If the formation of the two different nitriles is due to two different varieties of benzaldehyde, the benzaldehyde in the last case must have been transformed to the commercial variety during extraction because it yielded the same nitrile when treated with emulsin.

Since the *l*-amygdalin gave *l*-nitrile when treated with new emulsin, it seemed interesting to see what nitrile the *d*-amygdalin produced. Five grams of *d*-amygdalin and ½ gram of new emulsin were dissolved in 75 cc. of water and kept at 40° for 3½ hours. After the emulsin was precipitated and filtered out the solution was extracted with ether. When the solvent was evaporated to 20 cc. it was found to have an activity of -0.12° in a 2 dcm. tube. The nitrile was hydrolyzed with hydrochloric acid and the hydrolytic solution (15 cc.) had an angle of $+0.85^\circ$ in a 2 dcm. tube. Whether all the *l*-mandelonitrile in this case is a primary product of decomposition or a secondary product is hard to say, but it is exceedingly likely that a large part is a secondary product because the same nitrile is formed when *l*-amygdalin is used, where it must be secondary.

There seems to be only one other apparent explanation for the production of these two mandelonitriles, if one does not assume that there are two benzaldehydes. There might be something in the solution which added on in some way to the emulsin and this addition product might then synthesize the other optically active nitrile. Now the only substance present in both the hydrolysis of the *l*- and the *d*-amygdalin and not when the nitrile is synthesized from benzaldehyde and hydrocyanic acid is glucose. The following experiment was carried out to exclude this possibility:

Five grams emulsin and 2 grams glucose were dissolved in 25 cc. water

to which 25 cc. of hydrocyanic solution and 2 cc. benzaldehyde were added. After 3¹/₂ hours, the usual extraction was effected and the nitrile hydrolyzed with hydrochloric acid. The hydrochloric acid solution (50 cc.) showed a rotation of -1.45° in a 2 dcm. tube. The presence of the glucose, therefore, did not change the activity from dextro to levo.

Another experiment was carried out similar to the one above only substituting for glucose *l*-amygdalin, but the resulting mandelic acid was levo active.

Investigations will be continued on this subject to discover if possible the cause for the production of these two nitriles. The barks and leaves of wild cherry and elder berry will also be extracted to see if there is any difference in the emulsin produced.

In conclusion, I wish to thank Dr. Walker for proposing this investigation and for his suggestions and interest during its progress; also Dr. McIntosh for many practical suggestions.

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STUDIES ON ENZYME ACTION. I. SOME EXPERIMENTS WITH THE CASTOR BEAN LIPASE.

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This investigation was undertaken with the object of studying the action of a fat or ester splitting ferment (lipase) more particularly from the point of view of the ferment itself and its behavior under varying conditions. The lipase present in castor beans was chosen as most suitable for the present work.

The lipase preparation used in the experiments was prepared as follows: The castor beans¹ were ground roughly, extracted a number of times with carbon tetrachloride or chloroform,² then ground to a fine powder and passed through a 100-mesh sifter. In this way a large portion of the shells were separated. The fine powder was then extracted exhaustively with ether (100 times or more) in a Soxhlet extractor, practically all of the fat being removed in this way.³ The following experiment shows the activity of the preparation at the different stages: 2 cc. olive oil and 50 cc. water were treated with the substances stated for 17 hours at 38° and the acid present then titrated with a 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. No castor bean present = 0.6 cc. alkali required; 0.2 gram castor beans before sifting = 1.0 cc.; 0.2 gram castor beans after sifting (shells removed) = 1.9 cc.; 0.2 gram

¹ The castor beans were supplied by the Baker Castor Oil Company of New York.

² This extraction was carried out by Mr. C. W. Otto.

³ Cf. A. E. Taylor, *J. Biol. Chem.*, 2, 87 (1906), for the preparation of the lipase material from castor beans and a careful study of its properties.

castor beans after sifting and extraction with ether = 1.7 cc. This gives an approximate idea of the activity of the preparation. The olive oil used here was itself slightly acid in reaction and became more so on standing at the temperature in question in contact with water. The removal of the shells increased the activity markedly for the same weight of substance, as the shells do not contain the active constituent,¹ while the extraction with ether had very little effect, the slight decrease probably being due to the solubility of lipase in ether containing a fatty body, as Taylor pointed out.

In the experiments to be described, unless expressly stated to the contrary, no substance was added to the lipase mixture to increase the activity, either to form a more stable emulsion, increase the solubility, or act as activator.² No attempts were made to find the conditions for maximum action. The hydrolyses obtained are therefore, as a rule, smaller in magnitude than those found by others. Blank experiments were carried out with each series of experiments with lipase and ester, using lipase (and solvent) alone and ester (and solvent) alone; in this way corrections were introduced and the action of the lipase on the ester alone could be more closely approximated, although an uncertainty may be introduced by the possibility of a more complex action between lipase, ester and solvent aside from the hydrolytic action, compared with the sum of the actions of lipase and solvent and ester and solvent used as correction. The amount of ester hydrolyzed was measured in every case by titrating with a 0.1 *N* aqueous solution of sodium hydroxide, using 3–5 drops of a 1% solution of phenolphthalein in 95% ethyl alcohol as indicator and titrating to a distinct pink color. Owing to the presence of the solid suspension (lipase preparation), the end-point was sometimes difficult to determine, but in general the titrations were accurate to 0.1 cc. and in some cases where particular difficulty was encountered, to 0.2 cc.

The castor bean lipase preparation as used in the following experiments still contained a small proportion of shells. The preparation was light gray in color and on ignition gave a residue of white ash amounting to 9%. The preparation was slightly acid in reaction when mixed with water, 0.2 gram requiring 0.2 cc. 0.1 *N* sodium hydroxide solution for neutrality to be attained. The acidity increased slowly on standing, but whether this was due to a minute quantity of oil which had not been removed by the ether and which was slowly hydrolyzed, or to the slow

¹ Nicloux, *Mem. Soc. Biol.*, 56, 701, 839, 868 (1904).

² Cf. Rosenheim and Shaw-Mackenzie, *Proc. Lond. J. Physiol.*, 40, I, II, III, Feb., 1910, for the effect of emulsification with pancreas lipase and for the action of activators. Also Armstrong and Ormerod, *Proc. Roy. Soc.*, 78, 376 (1906), and others. Recently, Jalander, *Biochem. Z.*, 36, 437 (1911), followed the formation of the lipase-fat emulsion with the microscope.

decomposition of some of the substances present in the lipase preparation itself with the formation of acid, cannot be stated. In view of the long continued extraction with ether, the balance of probability would appear to rest with the latter view.

The general outline of the experiments performed for studying the hydrolytic action of the lipase preparation was as follows: Three esters were studied: methyl acetate, an example of a simple ester soluble in water; ethyl butyrate, which has been extensively used in investigations of this kind; and olive oil, as a substance closely related to the fats. After some comparative experiments in aqueous solution (experiments 1-12 in Table I), a number of experiments were carried out with different amounts of alkali added initially to determine what action, if any, the small amount of acid always present in the lipase preparation exerted (experiments 13-30). To test this point further, measurements were also made in moist ether, and acetone containing a small amount of water, both at the ordinary and at somewhat higher temperature (experiments 32-53). No experiment was allowed to last for more than 50 hours on account of the possibility of complicating the reaction by the continual increase in acidity of the lipase preparation itself.

Table I summarizes the results obtained. The first column shows the number of the experiment. Each experiment consists of three separate measurements, the results of which are shown in columns 7, 8, and 9. The amounts of substances used shown in columns 2, 3, and 4 refer in each experiment to the three sets of measurements. The esters used (column 2) were methyl acetate—MeAc—obtained from Kahlbaum and redistilled after treatment with sodium carbonate; ethyl butyrate—EtBu—purified by washing the ethereal solution free from acid and subsequent redistillation; and olive oil, the purest obtainable, and unless stated to the contrary, neutral in reaction before the experiment. The solvents are shown in column 3, moist ether referring to ether saturated with water at room temperature. Columns 4, 5, and 6 refer respectively to the weights of lipase preparation used, the duration of the experiments and the temperatures maintained. Columns 7, 8, and 9 show the experimental results found for each set of measurements, first with lipase, ester, and solvent, and then with ester and solvent alone, and with lipase and solvent alone. The numbers refer to the number of cubic centimeters of a 0.1 *N* aqueous solution of sodium hydroxide required to produce a distinct pink color with phenolphthalein. For the experiments in which ether or acetone was used as solvent, 50 cc. of water were added before the titration and the solution thoroughly agitated after each addition of alkali. A satisfactory end-point was obtained in this way. Column 10 gives the difference between the results in column 7 and the sum of the results in columns 8 and 9; that is to say, the amount

TABLE I.—THE HYDROLYTIC ACTION OF THE CASTOR BEAN LIPASE.

Expt. No.	Ester.	Solvent.	Lipase. Gram.	Time. Hrs.	Temperature.	Action in cc. 0.1 N sodium hydroxide solution.			
						Ester, lipase and solvent.	Ester and solvent.	Lipase and solvent.	Ester and lipase.
1.....	2 cc. MeAc	50 cc. water	0.2	17	38°	3.75	0.90	1.25	1.60
2.....	1 cc. MeAc	40 cc. water	0.2	23	38°	1.95	0.15	0.60	1.20
3.....	1 cc. MeAc	25 cc. water	0.2	42	20°	2.40	0.10	0.50	1.80
4.....	2 cc. MeAc	25 cc. water	0.5	42	20°	5.75	0.60	1.30	3.85
5.....	1 cc. EtBu	40 cc. water	0.2	23	38°	1.70	0.10	0.60	1.00
6.....	1 cc. EtBu	25 cc. water	0.2	50	38°	2.50	0.20	0.70	1.60
7.....	1 cc. EtBu	25 cc. water	0.2	50	20°	1.70	0.05	0.70	0.95
8.....	2 cc. EtBu	25 cc. water	0.2	48	20°	1.50	0.10	0.50	0.90
9.....	2 cc. EtBu	30 cc. water	1.0	48	20°	10.00	0.05	2.40	7.55
10.....	1 cc. olive oil	40 cc. water	0.2	23	38°	0.90	0.10	0.60	0.20
11.....	2 cc. olive oil	25 cc. water	0.5	42	20°	1.70	0.10	1.30	0.30
12.....	2 cc. olive oil	30 cc. water	1.0	48	20°	4.90	0.05	2.40	2.45
13.....	1 cc. MeAc	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	20°	1.40	0.10	0.15	1.15
14.....	1 cc. MeAc	25 cc. water, 0.2 cc. 0.1 N NaOH	0.2	42	20°	2.20	0.10	0.20	1.90
15.....	1 cc. MeAc	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	46	20°	2.00	0.10	0.20	1.70
16.....	1 cc. MeAc	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	38°	1.80	0.20	0.50	1.10
17.....	1 cc. MeAc	25 cc. water, 0.2 cc. 0.1 N NaOH	0.2	42	38°	2.30	0.30	0.90	1.10
18.....	1 cc. MeAc	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	46	38°	2.95	0.35	1.40	1.20
19.....	1 cc. MeAc	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	20	38°	1.75	0.20	0.40	1.15
20.....	1 cc. MeAc	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	44	38°	2.50	0.30	0.50	1.70
21.....	1 cc. MeAc	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	20	38°	1.65	0.30	0.30	1.05
22.....	1 cc. MeA	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	44	38°	2.40	0.35	0.35	1.70
23.....	1 cc. EtBu	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	20°	0.75	0.05	0.20	0.50
24.....	1 cc. EtBu	25 cc. water, 0.2 cc. 0.1 N NaOH	0.2	50	20°	1.50	0.05	0.50	0.95

25.....	1 cc. EtBu	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	38°	1.45	0.10	0.50	0.85
26.....	1 cc. EtBu	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	46	38°	2.10	0.10	1.40	0.60
27.....	1 cc. EtBu	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	20	38°	1.20	0.10	0.40	0.70
28.....	1 cc. EtBu	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	44	38°	1.55	0.20	0.50	0.85
29.....	1 cc. EtBu	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	20	38°	0.95	0.30	0.15	0.50
30.....	1 cc. EtBu	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	44	38°	1.10	0.20	0.35	0.55
31.....	1 cc. EtBu	25 cc. water, 0.2 cc. 0.12 N HCl	0.2	50	38°	3.20	1.20	0.70	1.30
32.....	1 cc. olive oil	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	20°	0.20	0.05	0.20	—0.05
33.....	1 cc. olive oil	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	46	20°	0.30	0.05	0.20	0.05
34.....	1 cc. olive oil	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	22	38°	0.80	0.10	0.50	0.20
35.....	1 cc. olive oil	40 cc. water, 0.2 cc. 0.1 N NaOH	0.2	46	38°	2.00	0.10	1.40	0.50
36.....	1 cc. olive oil	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	20	38°	0.55	0.10	0.40	0.05
37.....	1 cc. olive oil	40 cc. water, 0.27 cc. 0.1 N NaOH	0.2	44	38°	0.95	0.20	0.50	0.25
38.....	1 cc. olive oil	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	20	38°	0.45	0.10	0.30	0.05
39.....	1 cc. olive oil	40 cc. water, 0.45 cc. 0.1 N NaOH	0.2	44	38°	1.35	0.20	0.35	0.80
40.....	1 cc. MeAc	35 cc. moist ether	0.2	48	20°	1.40	0.20	0.60	0.60
41.....	2 cc. MeAc	40 cc. moist ether	1.0	48	20°	6.60	0.20	3.20	3.20
42.....	2 cc. MeAc	50 cc. moist ether	0.5	6 ¹ / ₄	35-40°	2.90	0.20	1.10	1.60
43.....	1 cc. MeAc	24 cc. acetone, 1 cc. water	0.2	48	20°	0.80	0.20	0.60	0
44.....	2 cc. MeAc	24 cc. acetone, 1 cc. water	0.5	42	20°	2.80	0.50	1.20	1.10
45.....	2 cc. MeAc	48 cc. acetone, 2 cc. water	0.5	4	56-60°	2.70	0.30	1.80	0.60
46.....	2 cc. EtBu	35 cc. moist ether	0.2	48	20°	0.80	0.20	0.60	0
47.....	1 cc. EtBu	50 cc. moist ether	0.5	6	20°	1.70	0.30	1.40	0
48.....	1 cc. EtBu	50 cc. moist ether	0.5	6	35-40°	1.50	0.20	1.30	0
49.....	2 cc. EtBu	40 cc. moist ether	1.0	48	20°	3.90	0.20	3.20	0.50
50.....	2 cc. EtBu	24 cc. acetone, 1 cc. water	0.2	48	20°	0.65	0.15	0.60	—0.10
51.....	2 cc. EtBu	27 cc. acetone, 3 cc. water	1.0	48	20°	4.40	0.15	3.90	0.35
52.....	2 cc. olive oil	40 cc. moist ether	1.0	48	20°	3.50	0.20	3.20	0.10
53.....	2 cc. olive oil	24 cc. acetone, 1 cc. water	0.5	42	20°	2.70	1.10	1.20	0.40

of action¹ between the lipase and the ester in the production of acid after subtracting the changes which the lipase preparation alone and the ester alone had undergone in the presence of the solvent. A few drops of toluene were added to each solution as antiseptic.

Before discussing the results shown in the table in detail, some general remarks may be made. The correction due to the action between ester and solvent is as a rule small (omitting experiment 31 in which a hydrochloric acid solution was used as solvent), exceeding 0.2 cc. in 9 cases out of 52 and 0.35 cc. in only 2 (experiments 1 and 4) in which ester was used which was originally slightly acid. The correction due to the action between lipase and solvent is more variable. This correction was determined in every case with some of the same lipase preparation used with the ester and made up with some of the same solvent, and treated in an identical manner. In this way it was hoped to introduce a more exact correction than if an average change of the lipase preparation with the solvent had been taken from a large number of separate experiments. It must be stated, however, that in two or three experiments (not given in the table) the lipase preparation after standing in contact with the solvent showed a very large increase in acidity, such as would give a considerable negative value for the action between lipase and ester. This only occurred in isolated cases and never for both parts of duplicate experiments carried on simultaneously. This change must therefore be considered as out of the ordinary and due to some unknown reaction in the lipase preparation. It is not considered further here, but the possibility of this occasional large increase must be kept in mind in considering any apparently exceptional experiment, as will appear later.

In (1)² the ester, methyl acetate, and lipase were slightly acid in character initially, making the correction terms rather large. The corrected action between lipase and ester is somewhat larger than that found in (2) but a strict comparison is not permissible as different amounts of ester and solvent were used. The results of (3) and (4) call for no special remark. With ethyl butyrate (5-9) the amount of ester used exerts no influence (7,8), doubtless on account of its limited solubility, and, with an excess present, constant concentration in solution. There is considerably less action than with methyl acetate, but a comparison with these results is impracticable. This can, of course, only be done satisfactorily with equivalent amounts of ester wholly in solution. With a larger quantity of lipase (9) there is more than a proportionately greater

¹ Strictly speaking, to this should be added the amount of alkali necessary to produce the same pink color with phenolphthalein, as this color was produced twice with the experiments in columns 8 and 9, and once with the experiment in column 7. This correction was not introduced, as the experimental error doubtless exceeds it.

² The numbers in parentheses refer to the numbers of the experiments in Table I.

action. With olive oil (10-12) there is much less action than with the simple esters, probably on account of its slight solubility.

Since, in these experiments, the lipase preparation was slightly acid in character, attempts were made to eliminate this acidity and to follow the action, starting with a medium neutral toward phenolphthalein.¹ As stated before, 0.2 gram of the preparation required 0.2 cc. 0.1 *N* sodium hydroxide solution. Three series of experiments were carried out with each ester and 0.2 gram of lipase preparation; one in which 0.2 cc. 0.1 normal sodium hydroxide solution were added initially (13-18, 23-26, 32-35); one in which 0.27 cc. were added (19-20, 27-28, 36-37); and one in which 0.45 cc. were added (21-22, 29-30, 38-39). Results were obtained for two-time intervals; 20-24 hours and 42-50 hours.

With methyl acetate and 0.2 cc. alkali (13-15) at 20° there is considerably more action (in the ratio of 3-2) for the time interval of 42 or 46 hours than for 22 hours. At 38°, however (16-18) there is the same apparent action for the two-time intervals, although the correction for the lipase-solvent action appears rather large for the longer intervals. This will be referred to again presently. With 0.27 cc. (19, 20) and 0.45 cc. (21, 22) alkali the action is practically identical with that observed at 20° and 0.2 cc. alkali, the ratio of the amounts of action being about 3 : 2 for the two-time intervals. Including the results of experiments 2 and 3, for an experiment lasting 20-23 hours, the amount of action was found to be 1.05-1.20 cc. alkali at 20° or at 38° in the presence or absence of initially added alkali in amount up to 0.45 cc. 0.1 *N* sodium hydroxide solution.² For an experiment lasting 42-46 hours, the action was approximately 1.80 cc. at 20° with or without 0.2 cc. added alkali and at 38° with 0.27 cc. or 0.45 cc. added alkali. Schütz's rule that with the same amount of enzyme material, the amounts hydrolyzed are proportional to the square roots of the times of action is approximately followed here; amounts hydrolyzed 3 : 2; times of action 2 : 1. The fact that at 38°, 42-46 hours and with 0.2 cc. NaOH solution added initially (16-18), the experiments (17-18) show no difference as compared with the action for 22 hours, in view of the results just discussed, throws doubt on these (17-18), results, and as the lipase-solvent correction is markedly higher here, this must be ascribed to experimental error, and as pointed out in the general discussion, to the high value for the lipase-solvent correction. Experiments 26 and 35 were carried on simultaneously with the same lipase-solvent blank, and the results obtained with these must therefore also be viewed with caution.

¹ Armstrong, *Proc. Roy. Soc.*, 76, (B) 606 (1905), studied the addition of various acids to the castor bean lipase and the dependence of the activity upon the acid added. This question was also studied by Connstein, Hoyer and Wartenberg, *Ber.*, 35, 3988 (1902), Hoyer, *Z. physiol. Chem.*, 50, 414 (1904) and others.

² Experiment (1) is omitted on account of the initial higher acidity.

With ethyl butyrate, somewhat different results were found (experiments 5-8 are included in this discussion). At 38° , for 20-23 hours, and for the amounts of alkali added of 0, 0.2, 0.27, 0.45 cc. (5, 25, 27, 29) the corresponding actions were 1.00, 0.85, 0.70, 0.50 cc. alkali, respectively. For 44-50 hours (6, 26, 28, 30) the actions were 1.60, 0.60,¹ 0.85, 0.55 cc., respectively. The addition of alkali evidently exerted a marked influence here. With none present, the ratio between the amounts of action for the two-time intervals was about the same as with the experiments with methyl acetate, obeying Schütz's rule, but the actions decreased and the differences between the amounts of action for the two-time intervals also decreased as the amount of alkali added initially was increased.

With olive oil, the amount of action for the shorter time interval was very small in every experiment (10, 32, 34, 36, 38), in no case exceeding 0.2 cc. alkali. The initial presence of alkali produced no apparent effect on the amount of hydrolysis. For the longer time intervals and 0.2 gram lipase preparation, the action varied from 0.05 cc. alkali at 20° (33), to 0.25-0.80 cc. alkali at 38° (35, 37, 39), with no apparent regularity as regards the amount of alkali added initially. A number of experiments were carried out in which the olive oil was used as an emulsion formed by adding its solution in a small quantity of acetone to the desired amount of water. The lipase preparation and either acid or alkali as desired, were then added and the further manipulations performed as in the other experiments. The results obtained showed no more satisfactory regularities than those which have been quoted with unemulsified olive oil, and are therefore not given in detail. In all these experiments with olive oil, whether emulsified or not, after adding the desired constituents, the mixtures were thoroughly agitated for a few seconds and then allowed to remain at the temperature in question until titrated (at the room temperature).

Experiment 31 is shown for the sake of comparison. The ester-solvent correction is large because of the hydrolysis of the ester by the hydrochloric acid. This correction is of doubtful accuracy, as the acid added to a lipase preparation, such as used here may well have been taken up by some basic body, resulting in a much smaller acidity than was used in the correction experiment.

In the experiments in which alkali was added initially, the weight of lipase preparation used required 0.2 cc. 0.1 *N* sodium hydroxide solution for neutrality to be attained. The first action of any added alkali doubtless would be to neutralize this small amount of free acid. Any further addition of alkali would, in the course of a short time, be neutralized by the acid formed by the saponification of the ester added

¹ This is the value from (26) and as stated before, is probably low (0.4-0.6 cc.).

(with the simple esters at any rate) or by the acid produced in some way from the lipase preparation (as made evident by the lipase-solvent experiments). Before this takes place, however, certain changes may be effected in the medium by the free alkali, such as the formation of an emulsion, temporary or permanent, or in the lipase preparation itself, and these unknown changes may influence the hydrolyzing power of the lipase. In the experiments with methyl acetate, alkali appears to exert no lasting influence on the amount of hydrolysis or acid formation from lipase and ester, as very nearly the same results were obtained whether alkali was added or not. This may have been due to the greater solubility of this ester as compared with the other esters, or to the rapid neutralization of the small excess of alkali added by the hydrolysis of the ester, removing the alkali before any permanent change was caused in the solution. With ethyl butyrate the results show a different action and evidently there is some direct influence of the alkali on the reaction. With olive oil the results do not point to any definite conclusion.

The small acidity of the lipase preparation represents the total free acids present and since these are doubtless organic acids,¹ the degree of ionization and therefore the H^+ ion concentration must be very small. In order to test the possible action due to the H^+ ions in a somewhat different way, some experiments were carried out in ether and in acetone solutions containing small amounts of water in which the small H^+ ion concentration would be expected to be very much decreased.

In ether saturated with water as solvent, (40) shows the action with methyl acetate to be about one-third as great as in aqueous solution (3). The action at 20° appeared to be approximately proportional to the weight of lipase preparation used (40-41). In (42), the solutions were boiled, using reflux condensers, and an amount of action was obtained in $6\frac{1}{4}$ hours at this temperature, $35-40^\circ$, about equal to the action which would have been obtained with the same weight of lipase preparation at 20° in 48 hours. In acetone containing small amounts of water (43-44) there was less action than in ether, but at 20° , with 0.5 gram of lipase preparation there was still considerable action in 42 hours. In (45) the solutions were boiled (reflux condensers) and in spite of the high temperatures of the boiling acetone solutions, a fair amount of action was shown.

With ethyl butyrate and ether saturated with water, or acetone containing water as solvent, action was obtained only when 1.0 gram of lipase preparation was used (49-51). With olive oil and these solvents (52-53), the action was only slight under the same conditions.

The extraction of the active constituent of the castor bean by water and by ethyl acetate was also studied.

¹ Mainly lactic acid according to Hoyer, *Loc. cit.*

Three grams of the lipase preparation were ground with 20 cc. of water in a mortar and filtered through a thin asbestos mat. The filtrate was yellow in color and clear, but on standing became opalescent. Portions of 2.5 cc. diluted with 25 cc. water and treated with methyl acetate for 18 hours at 38° gave the following results:

2.5 cc. extract 1 cc. MeAc 25 cc. water required 1.3 cc. 0.1 *N* NaOH.
 2.5 cc. extract 25 cc. water required 0.3 cc. 0.1 *N* NaOH.
 1 cc. MeAc 25 cc. water required 0.4 cc. 0.1 *N* NaOH.

The action was therefore found to be 0.6 cc. 0.1 *N* sodium hydroxide solution. Compared with experiments 1 and 2 in Table I, it is seen that the action is much less, especially when it is considered that a larger amount of lipase preparation was used. The same results was found by Taylor,¹ who stated that some lipase is contained in a solution after filtration through paper, but much less than in the original suspension.

The lipase preparation after the extraction with ether in the Soxhlet extractor was extracted for three days in the same apparatus with ethyl acetate. The solution after the extraction was yellow in color and contained a flocculent white substance in suspension. The ethyl acetate was evaporated under diminished pressure below 40° and the residue which was taken up with water formed a solution containing some white matter and a small amount of acid. This solution was divided into two parts (*a*) and (*b*) and tested with methyl acetate for 22 hours at 38° with the following results:

(*a*) 12.5 cc. water 2 cc. MeAc required 2.5 cc. 0.1 *N* NaOH.
 (*b*) 12.5 cc. water required 1.3 cc. 0.1 *N* NaOH.
 .. 15.0 cc. water 2 cc. MeAc required 0.4 cc. 0.1 *N* NaOH.

An acid formation equal to 0.8 cc. 0.1 *N* sodium hydroxide solution was found, showing that some of the active constituent had been extracted by the ethyl acetate. The residue from the extraction showed the same activity as unextracted lipase preparation, indicating that only a small part of the active substance had been removed.

The behavior of an aqueous suspension of lipase preparation toward an electric current was also studied. One gram of the lipase preparation was mixed thoroughly with 60 cc. water and placed in a U-tube of 1 cm. bore. The house current was passed through a 16 candle power carbon filament lamp and then through the solution in the U-tube, connection being made by means of platinum electrodes dipping just below the surfaces of the liquid in the two arms of the tube. It was evident that 0.5 ampere was not passing as the lamp did not glow at all, but that a small current was flowing was shown by the small but regular stream of gas evolved at the cathode. The current was allowed to flow for two weeks. After two days the solid matter had settled in the lower curved part of

¹ *Loc. cit.*

the tube except for a small amount which adhered to the electrodes or floated at the surface. Only occasional bubbles of gas were evolved at the anode. After two weeks, the solutions were removed separately from the two arms of the U-tube by means of pipets. They were slightly cloudy on account of the small amount of solid which had not settled to the bottom. Two portions of 10 cc. each were taken from each electrode solution, diluted to 35 cc. with water, 1 cc. methyl acetate added to one portion of each, allowed to stand for 47 hours at 38° and then titrated with 0.1 *N* sodium hydroxide solution. The results follow:

	Cathode solutions.		Anode solutions.	
MeAc.....	1 cc.	...	1 cc.	...
cc. 0.1 <i>N</i> NaOH required..	18.60	18.70	43.65	33.80

The cathode solution showed no hydrolytic power toward methyl acetate, although considerable acid was present there. On the other hand, the anode solution showed a still greater quantity of acid and also a large hydrolytic action. The absence of any but a minute gas evolution at the anode may therefore be explained as being due to some oxidation taking place there, and while some of the hydrolysis may have been produced by the large amount of acid formed, it seems very probable that the (negative) complex, produced or developed in part at any rate by oxidation, showed a marked hydrolytic or activating power.

Summary.

A comparative study was made of the hydrolysis of methyl acetate, ethyl butyrate, and olive oil caused by the castor bean lipase. The effect of adding small amounts of alkali at the beginning of the action was studied. No appreciable influence on the subsequent hydrolysis was found with methyl acetate, but with ethyl butyrate the action was different, depending upon the amounts of alkali added. Corrections were introduced in every case for the acid formed from ester-solvent and lipase-solvent.

In ether saturated with water, and acetone containing a small amount of water as solvents, methyl acetate was hydrolyzed to a considerable extent with lipase both at the ordinary and at more elevated temperatures.

Small amounts of an active constituent were extracted from the lipase preparation by water and by ethyl acetate.

By the electrolysis in water of the lipase preparation, a substance was produced in the anode solution, probably by oxidation, showing marked hydrolytic action.

NOTE.

The Combustion of Volatil Organic Liquids.—The writer in the course of the last few years has had occasion to make many analyses of volatil organic liquids. The determination of carbon and hydrogen by the familiar method originally devised by Liebig is fraught with serious practical difficulties when the compound to be analyzed has a low boiling point. The usual method in such cases has been to weigh out the liquid in a small bulb tube provided with a capillary, which after filling was sealed to prevent loss during weighing. The bulb was then placed in a boat, the tip of the capillary broken off, the whole then placed in the combustion tube in the furnace. By gradual heating of that part of the tube where the bulb was located, the liquid was slowly volatilized and burned. The carbon dioxide and water resulting from the combustion were collected and weighed in the usual manner.¹

The disagreeable features of this method are avoided by a new process which has been introduced and is now used in this laboratory. This new method is as follows: A combustion tube is drawn out at one end and a tube bearing a female ground glass joint is sealed on. That part of the tube which is within the heating zone of the furnace is now filled completely with coarse copper oxide held in place at the ends by suitable spirals made of copper gauze. The end bearing the ground glass joint protrudes about four inches from the end of the furnace, while at the other end, the combustion tube protrudes 3 inches or so, and to this end by a rubber stopper the sulfuric acid tube and potash bulb are attached in the usual fashion. The liquid to be analyzed is weighed out in a small U tube, which is fitted at the top of each arm with ground glass stoppers which close the end of the tubes, but which are perforated on one side by a small hole, which can be made coincident with the side outlet tubes simply by turning.

Thus each stopper serves to close the vertical tubes, also acts as a stop-cock to each side arm. To one side arm a rubber hose connection is made to a drying apparatus, while the other is fitted with a male ground glass joint, which just fits the ground glass end of the combustion tube.

To weigh out the liquid, the weight of the empty tube having been determined, one stopper is removed, the liquid introduced, best by a small pipet, and the stopper immediately replaced. No vaporized liquid can now escape as the tube is perfectly tight. It is best to previously lubricate the upper third of each stopper with a small amount of soft paraffin, the unlubricated space below wherever pervious is filled with air, forming an effective cushion to prevent absorption of vapor by paraffin, if the former is soluble.

¹ An excellent account of this process is given in Gattermann, "The Practical Methods of Organic Chemistry."

After weighing, the tube is connected to the combustion tube by the ground glass joint, the external fourth being lubricated by a very small amount of soft paraffin, while to the other side arm of the U tube the drying apparatus is connected. The combustion tube has meanwhile been thoroughly ignited and is now red hot. The two stopcocks of the U tube are now turned so as to permit a stream of pure dry air (from the usual purifying apparatus) to stream over the surface of the liquid to be burned. The vapor, mixed with the excess of air used, passes through the combustion tube, and over the red hot copper oxide, while the resulting water and carbon dioxide are caught in the customary sulfuric acid tube and potash bulb. If the liquid has a low boiling point like ether, it is well to immerse the lower end of the weighing tube in cold water, to prevent the ether from volatilizing too rapidly. With acetone, neither cooling nor warming is necessary. For a liquid boiling at 100 to 125°, it is best to heat the U tube to 50 or 60° by immersing the lower part in a beaker of warm water.

This method is rapid and accurate and since it is not necessary to allow the furnace to cool between each analysis, several combustions can be made in a single day.

Before using this apparatus for the analysis of hydrocarbons, it was tried out with acetone.

The acetone was purified by drying thoroughly with calcium chloride, and subsequently distilling, using a large Le Bel Henniger fractionating column. The sample taken for analysis boiled at 56° under 760 mm.

Subst., 0.3645, 0.1471; CO₂, 0.8260, 0.3361; H₂O, 0.3302, 0.1303.

Calculated for C₃H₆O: C, 62.07; H, 10.34

Found:	I.	II.
C.....	61.80	62.30
H.....	10.06	9.85

Analyses were next made of an octane (boiling point, 118.8–119°), and octylene (boiling point, 119.6–120.5°), which had been obtained in a hydrocarbon research.

Subst., 0.3157; CO₂, 0.9868; H₂O, 0.4089.

Calculated for C₈H₁₈: C, 85.62; H, 14.38.

Found: C, 85.27; H, 14.37.

Subst., 0.2935; CO₂, 0.9012; H₂O, 0.2935.

Calculated for C₈H₁₈: C, 84.10; H, 15.90.

Found: C, 83.74; H, 15.74.

LATHAM CLARKE.

CAMBRIDGE, MASS.

NEW BOOKS.

J. H. van 't Hoff's *Amsterdamer Periode, 1877-1895*. By DR. W. P. JORISSEN, Lektor a. d. Univ. Leiden and DR. L. TH. REICHER, Priv. Dozent a. d. Univ. Amsterdam.

This well written, well printed, and copiously illustrated little book of 106 pages does not pretend to be a complete biography; the story of van 't Hoff's life has been told so often and so recently that the authors are justified in treating most of it as well known, and have contented themselves with adding chapters from their personal recollections, and quotations from relatively inaccessible Dutch publications.

A section is devoted to the establishment, in 1785, of a professorship of Chemistry in Amsterdam, and sketches of those who have filled the chair and the conditions under which they worked. As appendix, four little known articles by van 't Hoff are republished, all of autobiographical interest: one in memory of his predecessor Gunning, two to mark the doctor-jubilees of his students van Deventer and Reicher, and a third "Die Verwirklichung einer Vorhersagung in einer Rektoratsrede" which gives a brief description of his life and work in Berlin.

Quoting Carlyle, the writers say: "We cannot look, however imperfectly, upon a great man, without gaining something from him," and these stories of life in the laboratory and of the personal relations of van 't Hoff with his colleagues and students, even the undergraduate criticism of his lectures taken from the students' yearbooks, help us know van 't Hoff as something more than a contributor to the *Z. physik. Chem.*; his two former assistants deserve our thanks.

Bibliographies of van 't Hoff's books, pamphlets and papers, and of the dissertations from his laboratory in Amsterdam, and a list of biographical sketches and articles on van 't Hoff and his work close the book.

W. LASH MILLER.

"Higher Mathematics for Chemical Students." By J. R. PARTINGTON. Methuen & Co., London. 1911. pp. 279. Price, 3 s. 6 d.

Chemistry has always made great use of symbols but it is nevertheless true that chemists have all too frequently objected to the use of mathematical symbols or failed to use this most valuable scientific aid in their investigations. Text-book writers frequently explain that, in their books, as little use of the calculus has been made as possible. This is, however, a situation in chemistry which is rapidly passing. Comparatively few students, who have taken the regular college courses in mathematics, can apply their knowledge to scientific problems, and the appearance of the Nernst-Schoenflies "Einfuehrung in die mathematische Behandlung der Naturwissenschaft" in 1895 was a welcome text as indicated by the fact that it is now in the sixth edition. Mellor, in his "Higher Mathematics for Students of Chemistry and Physics," has given us a book which

is particularly rich in examples of the application of higher mathematics to scientific data and problems. Mellor's book also contains considerable thermodynamics and many mathematical tables and is fairly complete, so that it is a valuable handbook. Along these same lines we now have this book on "Higher Mathematics for Chemical Students, by J. R. Partington. It is clearly written and not too formidable a book, so that it must be really interesting reading to students who have not connected their mathematics and experimental data and problems. The book is distinctly an addition to the texts that the chemist must use. It seems to the reviewer that more attention should be given to the theory of probabilities in its application to the questions of errors of measurements and the question of judgment in interpreting results, indeed a valuable and interesting book might be written along these lines.

G. A. HULETT.

Contemporary Chemistry. By E. E. FOURNIER D'ALBE. pp. xvi and 180. New York, 1911: D. Van Nostrand Co. Price, \$1.25.

This book is, in the author's words, "intended to give a bird's-eye view of the whole field of modern chemistry." "It is proposed to outline the laws, conceptions, and ideals underlying the new chemistry, to show where they are at variance with Physics, and where the bridge between the two sciences has already been thrown."

The reviewer attaches high importance to conscientious efforts to present in popular and readable form the results of scientific research and the present ambitious work certainly possesses, in an unusual degree, the excellent quality of readability. It, moreover, gives evidence of a very wide familiarity with the immense field which the author endeavors to cover. The style is colloquial and lively, but it must, with regret, be noted that the effort to make it so is sometimes forced and not infrequently leads to serious literary defects. It is only possible to point out a few passages illustrating some of the latter. "..... We are still some distance off a plausible theory of spectra." (p. 31) "..... We at once get optically active forms, implying a tri-dimensional¹ arrangement." Speaking of the ignition of thermit, the surprising statement (p. 135) is made: "An intense combustion is the result, in the course of which the aluminium deprives the iron of its oxygen, and the latter escapes at a white heat." "Had that mind been free from the incubus of authority the 'call of the wild' might have been irresistible even then. But there was Plato and Aristotle; there was the elaborate syllogistic system of scholasticism, prepared to crush and devour all virgin thought in its powerful jaws" (p. 14).

¹ Asymmetric is meant. The reference is to molecules of optically active carbon compounds.

"The phlogistic doctrine was now tottering to its fall. The man who knocked it down was Lavoisier" (p. 16).

"At the absolute zero of temperature, illustrated by the graveyard, there would be evidence of crystallization in the quadratic system" (p. 3).

Professor Loeb might object to this: "If carbon is still to be quadrivalent—and no organic chemist except Gomberg will hear of anything else."

A few dubious statements are made, which should receive the author's attention in case of the issue of a new edition. Thus (pp. 135–136), we read *à propos* of the manufacture of aluminium:

"If it were possible to use bauxite instead of cryolite, the process of obtaining aluminium would be much cheapened; That event will mark a new era." Other similar instances may be found at pp. 20 and 128 (foot).

The theory of osmotic pressure as presented on pp. 65–66 appears open to serious criticism. The statement (p. 141) that "The rarity of ancient specimens of glass proves that glass devitrifies in a few centuries," rests on a kind of logic that one hardly expects to find in a scientific book, and the reference (p. 27) to "Ramsay's noble gases, Argon, Crypton, Xenon" is unjust to Lord Rayleigh.

In conclusion it is not too much to say that "Contemporary Chemistry" is the most interesting work of its kind that has appeared for many years and is marked by wide learning and by a vivid style of treatment.

LAUNCELOT W. ANDREWS.

Experiments in General Chemistry. By W. S. HENDRIXSON. Printed at Grinnell, Iowa. pp. 64 and 14 figures.

A collection of 157 experiments covering the common elements and their compounds. There is no remarkably new mode of attack, nor originality in the choice of the experiments described, while those covering the metals are too largely restricted to the information that would be acquired in a course in qualitative analysis. Experiments on chlorine and carbon monoxide are described without any warning as to the poisonous nature of the materials. As a whole the experiments are well chosen and well adapted to an elementary course, though there is a lack of quantitative experiments, and of those questions which may serve to induce a scientific curiosity.

H. ISHAM.

Stand und Wege der analytischen Chemie. By W. BÖRGER. xiii Band der "Die chemische Analyse." Ferdinand Enke, Stuttgart. pp. 53. Price, M 1.80.

This little pamphlet is introductory to the general subject of analytical chemistry and was suggested by an article on the present condition of analytical chemistry by W. F. Hillebrand which was published in

THIS JOURNAL, 27, 300. The author first reviews the history of this branch of chemistry, particularly the attitude taken by great chemists of the past towards analytical chemistry. Second, the general principles underlying gravimetric and volumetric analysis are discussed and it is shown how various principles of physical chemistry may be applied to improve analytical methods and to explain results.

The paper shows the importance of analytical chemistry as a dignified branch of the great science and emphasizes the need of placing this branch upon a sound scientific basis. The paper is well worth reading as the subject is admirably treated.

O. L. SHINN.

A Textbook of Practical Chemistry for Technical Institutes. By A. E. DUNSTAN, D.Sc. (London), Head of the Chemical Department, East Ham Technical College, and F. B. THOLZ, B.Sc. (London), F.C.S., Lecturer in Organic Chemistry, East Ham Technical College. With numerous diagrams. Methuen & Co., Ltd., London. September, 1911. Crown 8vo., pp. viii + 335. 3 s. 6 d.

This book is one of Methuen's Textbooks of Science, for "Secondary Schools and Schools of Science." It is intended as a guide to laboratory work and is very generally amplified by brief but careful discussions of the theory connected with the experimental work in hand. The resulting correlation of laboratory and lecture work cannot avoid being helpful to the student. The immediate object in writing the book has been to collect in one moderate priced volume the experimental chemistry usually performed by students in the modern English technical school, most of whom find the various treatises used, too expensive. In this laudable purpose great success has certainly been achieved and the book should also be a most useful reference volume to the student.

The contents comprise: "Dry tests" (11 pp.). A now a days much neglected art in the study of chemical substances. The common inorganic compounds are examined systematically after the manner of determinative mineralogy. "Reactions of the ions" (89 pp.). The extent of the work in qualitative analysis is shown by the fact that among the negative ions considered are such cases as aluminate, zincate, stannate, persulfate, dithionate, silicofluoride, borofluoride, and permanganate ions. "Group analysis" (21 pp. including "analysis for negative ions"). "Reactions of the 'rare' elements" (14 pp.). "Volumetric analysis" (29 pp.). "Gravimetric" and "complete analysis" (35 pp.). "Simple gasometry" (10 pp.). "Organic section" (79 pp.), including: tests for elements in organic compounds; quantitative estimation of elements; common organic estimations; common operations in organic preparations; identification of simple organic substances (30 pp.); "Physico-chemical determinations" (23 pp.); Appendix (18 pp.), consisting of tables of solubilities, preparation of reagents, atomic weights, logarithms, specific gravity, boiling and melting points, etc.

It is noticeable that in the determination of silica but a single evaporation is recommended. There appear, however, to be few such objectionable procedures. The precautions to be noted are very clear and, especially in the early portion of the book, excellent. Full page charts are printed which start the student from some common substance, such, for instance, as the mineral chromite when studying the reactions of chromium. The steps are indicated on the chart whereby the student is to proceed from the mineral to the various important compounds, performing as he goes along the common reactions required for qualitative analysis, thus blending inorganic preparation work with the qualitative study of reactions. The other chapters of the book seem equally as practical. Mineral analysis, it is cheerful to note, will not be a lost art with the student who completes the analytical exercises of this volume.

JAMES R. WITHROW.

Traité Complet d'Analyse Chimique Appliquée and Essais Industriels. Par J. POST and B. NEUMANN. Deuxième édition française entièrement refondue. Traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. Chenu, M. Pellet. Tome troisième, premier fascicule. Engrais commerciaux, amendements et fumiers—terre arable et produits agricoles—air—huiles essentielles—cuir et matières tannantes—colle—tabac—caoutchouc et gutta-percha—matières explosives et allumettes. Avec 56 figures dans le texte. Paris: Librairie scientifique A. Hermann et Fils. 1912. pp. 1-468.

Brief notices of earlier instalments of this book have already been published in *THIS JOURNAL*, 30, 912; 31, 120. The book must, naturally, be compared with Lunge's "Untersuchungsmethoden," somewhat to the advantage of the latter. This may not be entirely fair, however, for the two works do not cover exactly the same ground, and the matter presented by Post and Neumann is undoubtedly excellent and up-to-date. The chief fault seems to be a lack of proportion in subdividing the book. The extremes in the present fascicle are Explosives and Matches, which occupy 135 pages, while "Arable Soil and Agricultural Products" are disposed of in 7 pages. Perhaps this only shows that the authors and the reviewer have different ideas about book-making. C. E. WATERS.

Die Kolloide in Biologie und Medizin. By H. BECHHOLD. Dresden. 1912. xii + 441 pp. Theodor Steinkopff, publisher. Price, bound, 15.50 Marks.

For all dimensions of matter, from those of atomic systems to those of world systems, the laws of form and stability have been carefully studied and, in general, well defined. Only systems whose parts are in size, roughly speaking, between the dimensions of the molecule and those of particles easily visible with the ordinary microscope, still defy simple general treatment. These are the colloids, the ultimate morphological elements, according to the ordinary conception of the term morphology, of the living cell. Biology, accordingly, is especially delayed by the fail-

ure of the physical sciences to elaborate a simple method of dealing with the colloids, such as the laws of solution provide for molecules, such as structural chemistry provides for the arrangement of atoms.

The new work of Bechhold, himself an accomplished investigator of the role of colloids in biology, seeks so far as possible to obviate such difficulties by providing a systematic treatment of this subject, and the author has been on the whole remarkably successful in his difficult enterprise.

The book is divided, according to a plan at once convenient and logical, into four parts—first, an introductory discussion of theory, general physico-chemical facts, and methods of investigation, secondly, a description of the colloidal constituents of living organisms and their products, thirdly, a discussion of the organism as a colloidal system, and finally, a discussion of toxicology, pharmacology, and the microscopist's technique in their relation to colloids.

In the present state of knowledge it is impossible for such a work to possess any characteristics of finality. But the author, squarely facing the necessity of being at times superficial and at other times of substituting possible suggestions for missing facts, has managed to combine a great variety of information in such manner as will render it available to many workers in biology and medicine and help them to a clearer understanding of some of the great problems of both the statics and dynamics of living matter.

Especially satisfactory is the simple treatment of theory, including the theory of adsorption. The simplifying explanations of phenomena are extracted from the theories, but at the same time great care is taken to avoid rigid application of theories of processes too complicated for such treatment at the present time.

The work contains considerations of many different data and theories of varying merit, and there are among them, no doubt, a certain number which will be subject to revision in the future; but such is one of the difficulties of the pioneer. It is to be hoped that this work will, through future editions, grow up with the subject, for it fills a most important place in scientific literature.

L. J. HENDERSON.

Handbuch der Mineralchemie. Vol. I, No. 5. By DOELTER, *et al.* Theodor Steinkopff, Dresden. M. 6.50.

This number of "Mineralchemie" completes the subject of mineral melting points and the influence of pressure on them. A comprehensive table of silicate melting points, so far as they have been determined, is included. Other important physical properties of the silicates, *viz.*, latent heats, specific heats, thermal and electrical conductivities, viscosities and volume changes in melting are then considered. The data

belong to different periods of development and are of all degrees of value, but the scarcity of reliable data is everywhere evident. The present state of our knowledge is sometimes satisfactorily summed up, and sometimes otherwise. The latter portion of the book is given up to the consideration of binary systems of the silicates. Here some highly fantastical diagrams might well have been omitted. In connection with these silicate systems are discussed some highly interesting geological questions, such as natural eutectics, resorption and zonal structure, the order of crystallization from magmas, the application of the phase rule to the eruptive rocks, and the structure of the latter.

E. T. ALLEN.

The Technology of Bread-making, Including the Chemistry and Analytical and Practical Testing of Wheat, Flour, and Other Materials Employed in Bread-making and Confectionery. WILLIAM JAGO, F.I.C., F.C.S., AND WILLIAM C. JAGO. American Edition. Bakers' Helper Co., Chicago, 1911. pp. 908 + viii. Price, \$6.50.

This cyclopaedic volume is the outgrowth of the earlier and smaller editions which appeared in 1886 and 1895 on the same subject from the pen of the senior author and the mode of treatment of the present volume is, in general, the same as that of the earlier editions. The scope of the work is even greater than is indicated by the title and sub-title as a glance at the table of contents shows. The book might really be divided into several parts, the first of which deals with matters of general Chemistry, Physics and Biology for here we find chapters on Inorganic and Organic Chemistry, the Microscope and Polarization of Light, Mineral and Fatty Matters, the Carbohydrates, the Proteins, Enzymes and Diastatic Action, Fermentation, Bacterial and Putrefactive Fermentation, Technical Researches on Fermentation and the Manufacture of Yeasts. The first twelve chapters, therefore, occupying 253 pages, deal for the most part only in an indirect way with the subject in hand, serving as a storehouse of fundamental chemical and biological knowledge. Obviously, the treatment of some of these subjects is brief, simple and rather one-sided, the intention being to supply just those facts which are necessary for the thorough understanding of the later technical details.

The second part, chapters 12-18, deals with the structure and physiology of wheat grain, chemical composition of wheat, strength of flour, many tables of analyses of various products of milling and the bleaching of flour.

What may be called part three, chapters 18-22, takes up the subject of bread-making, special breads, and bread-making processes, bread improvers and a general discussion of the nutritive value and digestibility of various breads, with a chapter on the weighing of bread. Another short section, chapters 23-24, treats of bake-house design and the machine

bakery and its management and goes exhaustively into the architecture and mechanical equipment of bakeries.

The remaining nine chapters, with the exception of the last, describe analytical methods, bread analysis, adulterants and their detection and routine mill tests. The last chapter discusses confectioners' raw materials, especially substances used in the making of other products than bread.

One is surprised and almost overcome at the size of this work. A cursory examination of it suggests that much of the material in the first seventeen chapters might be condensed and a part of it omitted, and this belief is strengthened by careful reading. One wonders why it should be necessary to devote so much space to General Chemistry, Physics, etc., when there are so many elementary books on the subject which give the reader a somewhat broader view. This seems to be, however, one of the class of books in which no previous knowledge is taken for granted. This over-expansion is perhaps the most serious fault that can be charged to the book, as the descriptions in the preliminary chapters are in general clear and the statements accurate. Occasionally there is a statement which may be questioned, a term used which has a double meaning where modification could make the meaning perfectly evident. An example of this is found on page 31 where the term chloride of lime is used when hypochlorite is meant. Another unimportant criticism may also be made in that there is frequently unnecessary detail in description, as for example, under the head, "How to Use the Microscope," we find this statement, "To commence using the microscope remove it from the case" This is but one of numerous occurrences of this sort. While this detail may be necessary in some quarters in order that directions may be followed carefully, the general effect on the trained reader is to lessen interest and make the volume tiresome. The data of analyses and other investigations which were presented in the older volumes have been practically retained with the addition of more recent results. It may be fairly questioned whether analytical data obtained as far back as 1852 are of real value as compared with similar data obtained within the last five years, especially in view of the great improvement in certain methods of analysis.

In the chapter on proteins the official nomenclature recently adopted is set forth and the results of much of the new work on vegetable proteins are given in an excellent way. After such concise and up-to-date account of the proteins, one is surprised to find at the end of the chapter a paragraph on the nature of putrefaction which presents an old and long since abandoned view, for in it one finds no mention of bacteria as inciting causes and the inference is that air is responsible. I quote, "It would thus appear that putrefaction is not a process appertaining exclusively

to the grain itself, but is in some way dependent on the action and presence of air."

The chapters dealing with yeast and fermentation are in general clear and excellently presented, except for some vagueness regarding the difference between "high" (top) and "low" (bottom) yeasts. In the reviewer's opinion the chapter on Bacterial and Putrefactive Fermentation is the poorest in the book as it contains many inaccuracies and misstatements. To include the bacteria under the caption "Moulds" is inexcusable, and there is a lack of exactness or looseness of statement pervading the whole chapter.

We may summarize the situation by saying that the chapter is not up-to-date and presents an antiquated view of this subject.

When, however, the authors attack the real subject of bread and bread-making it is at once apparent that they are on familiar ground and masters of their art and the results are correspondingly gratifying. The book then becomes a veritable mine of information especially on the English procedures and practically all important researches on bread and bread-making are cited or referred to. All kinds of breads are treated, special methods are described in detail and the subject treated in a most thorough and exhaustive manner. This portion of the volume cannot fail to be a most valuable book of reference for all who are engaged in the baking industry.

The chapters on the commercial testing of wheat and flour and the methods of analysis present a great variety of analytical methods. Some of these differ in certain respects from the standard methods of the official agricultural chemists but it is at least interesting to have such a variety of methods of analysis collected in one reference volume.

From the standpoint of book-making the volume is attractive, the printing is good, important sentences or statements are printed in heavy type and thus made prominent and easily found, and typographical errors are rare. Except, therefore, for the fact that there seems to be a lack of concentration, the volume must be regarded as of the highest value and easily the most authoritative work upon the subject.

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THE SEPARATION OF THE RARE EARTHS.

By C. JAMES.

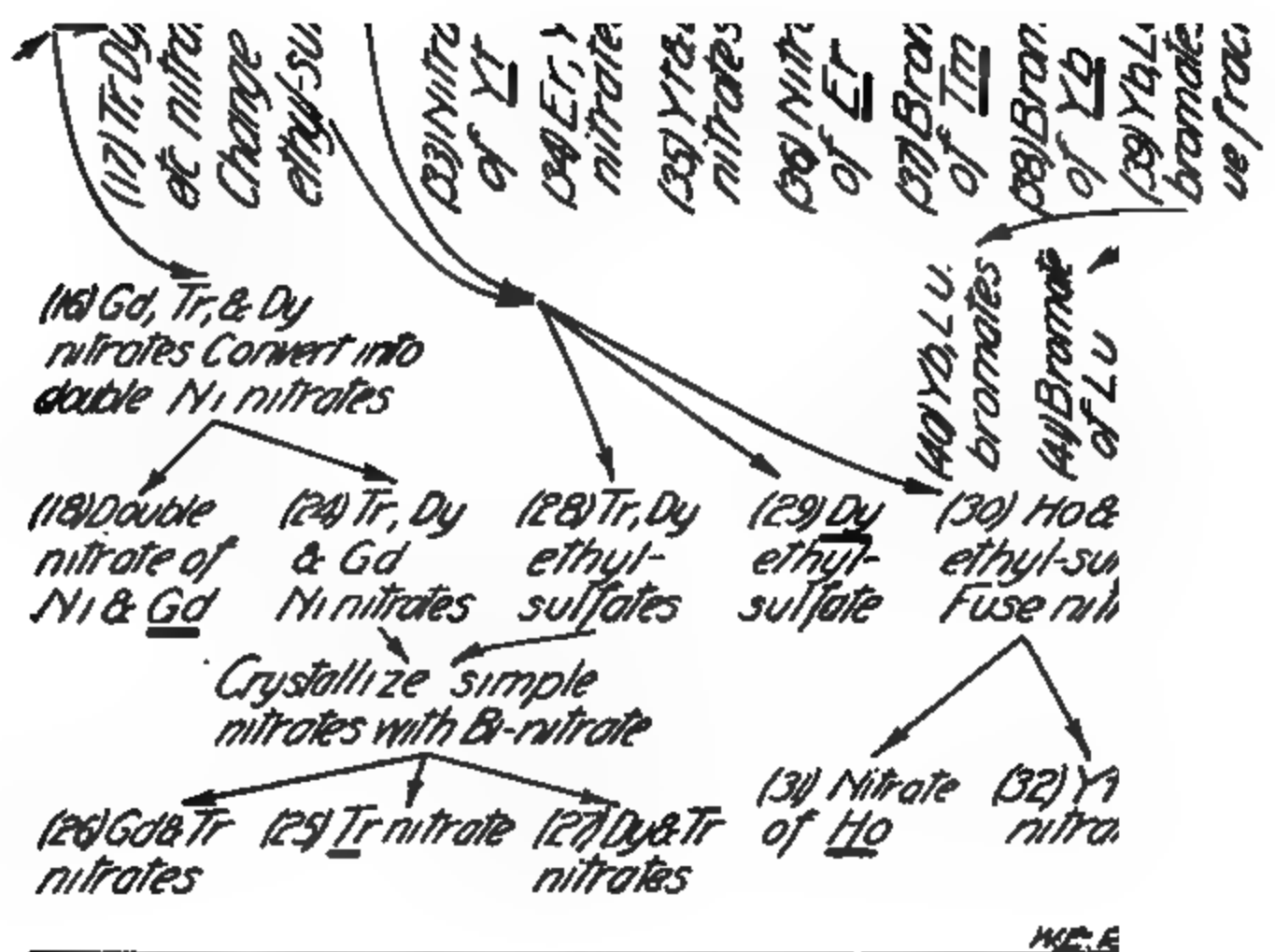
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Since writing a scheme for the separation of rare earths in 1908, many new methods have been introduced and others modified. Furthermore, since communications asking for reprints still arrive, the author has considered it advisable to bring the methods of separation up to date.

The operations herein dealt with concern only the rare earth elements, La, Ce, Pr, Nd, Sm, Eu, Gd, Tr, Dy, Ho, Er, Tm, Yb, Lu, and Ct together with Yt and Sc, it being considered that other metals, such as thorium, zirconium, etc., have been removed, if found occurring in the oxalate precipitate. A description of the working up of rare earth minerals will be found included in a paper on thulium.¹

There are four different methods for attacking the crude oxalates, which depend upon the composition of the latter: (a) If the mixture is chiefly composed of lanthanum, much cerium, praseodymium, neodymium, samarium, europium and gadolinium, it should be converted into the neutral nitrates and boiled with potassium bromate and marble, as required for the separation of cerium. (b) If only a little cerium is present, the oxides should be converted into double magnesium nitrates, which are then fractionated, the cerium being separated from the fractions where it is found to occur. (c) Should the mixture be composed of gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, yttrium and scandium it is best to commence with the fractional crystallization of the bromates. (d) When the cerium and yttrium metals occur together, one must commence with the sodium sulfate treatment, which is the first operation shown on the diagram.

¹ THIS JOURNAL, 33, 1332.



Separation of Yt and Ce Group.—The solution in the form of the chloride or sulfate is stirred with sodium sulfate crystals until the praseodymium and neodymium bands disappear. Sodium sulfate is better than potassium sulfate when used with care. The solubilities of the yttrium earth sulfates increase with the addition of sodium sulfate until the latter reaches a certain concentration, after which the former rapidly decrease. When all the cerium group double sulfates (1) are precipitated, they are filtered off and washed with sodium sulfate solution. The filtrate is acidified, and the rare earths thrown out by means of oxalic acid (2).

Separation of Ce.—The double sodium sulfates (precipitate 1) are boiled with strong sodium hydroxide until thoroughly decomposed. The mass is diluted, filtered and washed with boiling water until free from sulfates. The hydroxides are dissolved in nitric acid, the solution made nearly neutral, heated to boiling and potassium bromate added.¹ When the red fumes of bromine make their appearance, a few lumps of marble are added to keep the liquid nearly neutral. (Recent experiments show that powdered marble, added very gradually, can be used with great advantage, when working upon the large scale.) The whole is then boiled until some of the filtered liquid fails to give the hydrogen peroxide test for cerium. The marble (if in the lump condition) is removed and the precipitate of basic ceric salts is allowed to settle as much as possible, after which it is filtered off and washed with water acidified with nitric acid (precipitate 3). The filtrate can either be precipitated in the cold by oxalic acid, or else heated to boiling and the hydroxides separated by means of an excess of sodium hydroxide. The hydroxides or oxalates form precipitate 4. In case oxalic acid is used to throw out the rare earths, it is advisable not to use too much potassium bromate in the early part of the operation, as otherwise much oxalic acid is used up by the oxidation and quantities of bromine are liberated. When large quantities of cerium are present, the boiling should be continued until only a little remains in solution; under these conditions the cerium basic salt, after washing with acidified water, is obtained in a very pure state. The small amount of cerium remaining in solution can then be removed by continuing the boiling as described above.

If necessary, the cerium can be purified by repeating the process, or as follows: The precipitate is dissolved in concentrated nitric acid by the aid of a *very little* alcohol. The orange red liquid obtained in this manner is diluted, and boiled with lump marble. The solution must not be allowed to become alkaline by boiling too long. The precipitate is filtered off and the solution is then treated with potassium bromate, etc., to remove the remaining portion. The basic salts may be further purified by dissolving in hydrochloric acid, adding a slight excess of sulfuric

¹ James and Pratt, *THIS JOURNAL*, 33, 1326.

acid and heating. The crystallin cerium sulfate is separated, and washed with alcohol. The sulfate is then rendered anhydrous, made into a cold saturated solution, and the pure hydrated sulfate thrown down by heating.

Separation of La Group.—The cerium-free earths (4) if in the state of oxalates are ignited to oxides. For roughly separating these earths upon the large scale the crystallization of the double magnesium nitrates is employed. These compounds crystallize more readily than the double ammonium nitrates. The magnesium double salts,¹ $2R''(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by magnesium oxide, after which the two solutions are mixed and evaporated until, upon blowing on the surface, small crystals form. Water is sprayed over the surface and the whole allowed to crystallize for about twenty-four hours. The mother liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learned by experience. Both fractions are again allowed to crystallize for a like period, the concentration being such that half of the solid separates upon cooling. In the subsequent fractionations the more soluble moves in one direction and the less soluble in the opposit. After the crystallization of the second series is complete the liquid from the most soluble portion is poured off and evaporated, while the liquid from fraction I is used as the solvent for the crystals forming fraction II, water being added or evaporated as may be necessary. The least soluble portion, fraction I, is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one series of operations and then be added to the next lot.

After a few series of crystallizations, the least soluble portion becomes very light colored, later growing nearly colorless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein; in other words, fractions of the same color are united.

The most soluble portion changes very rapidly. It soon takes a yellow color and shows a samarium spectrum together with the bands of dysprosium, holmium and erbium. Sometimes at this point the liquid refuses to crystallize or else a precipitate may form. If either of these things happens, it is best to dilute with water and precipitate with oxalic acid in order to separate the impurities that have accumulated and interfere with the crystallization. The insoluble oxalates are converted back to the double magnesium nitrates in the same manner as already described.

¹ Demarçay, *Compt. rend.*, 130, 1019.

The neodymium bands finally become very weak in the mother liquors from the most soluble fractions. These are then set aside for the preparation of samarium, europium and gadolinium. When the samarium has been separated the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst and when this occurs, it is separated from the rest as crude neodymium. After the process has been continued for some time longer, it will be found that the material has been split up into four groups according to the order of their solubilities. Commencing with the least soluble we have: (5) Lanthanum and praseodymium magnesium nitrates. (6) Praseodymium and neodymium magnesium nitrates. (7) Crude neodymium magnesium nitrate. (8) Samarium, europium and gadolinium magnesium nitrates together with the simple nitrates of terbium, dysprosium, holmium, yttrium, etc.

Separation of La.—Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach¹ which consists of the fractional crystallization of the double ammonium nitrates of the type $M''(NO_3)_3 \cdot 2(NH_4NO_3) + 4H_2O$. These compounds are crystallized from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. The double salts are obtained by dissolving the oxides in the required amount of nitric acid, and for every three parts of acid required for the oxides two additional parts are neutralized by ammonium hydroxide. The resulting solutions are mixed, filtered if necessary, and evaporated until small crystals form on blowing over the surface of the liquid. A little water is then sprayed over the hot solution and the whole set aside to crystallize. The time required for large amounts is about twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. The lanthanum is rapidly obtained in a colorless condition. A saturated solution gives no praseodymium absorption spectrum even when very thick layers are used. The lanthanum ammonium salt encloses only a small amount of mother liquor, while the double magnesium compound carries large quantities. Both cerium and praseodymium pass into the more soluble fractions (10).

The lanthanum may be further purified by dissolving in water and precipitating by means of oxalic acid. This oxalate is treated with a slight excess of sulfuric acid, and the whole gently ignited until nearly all the free acid has been driven off. The sulfate is powdered and dissolved in water at about 1° , with rapid stirring, until the liquid becomes saturated, after which it is filtered and placed in a water-bath which is gradually raised to about 32° . The solution rapidly becomes solid, owing to the separation of hydrated lanthanum sulfate. It is filtered upon a Büchner funnel and washed with hot water. The small quantity that

¹ *Monatsh.*, 6, 477.

remains in solution is then thrown out by means of oxalic acid. The crystallized sulfate may be again converted into the anhydrous state by heating, and the solution of this, prepared in the cold, precipitated by heating again. This lanthanum material (9) should give a fine white oxide.

Though the crystallization of such compounds as the metanitrobenzenesulfonates and bromates may give satisfactory results, the old method of Auer von Welsbach is the best general procedure.

Separation of Pr.—Praseodymium can be obtained from two sources: (a) From the more soluble lanthanum fractions (10). (b) From the mixed praseodymium and neodymium double magnesium nitrates (6). These are treated separately. Praseodymium containing lanthanum is purified by continuing the fractional crystallization of the double ammonium nitrates. The process is continued until no more lanthanum ammonium nitrate separates from the less soluble portions of the series. In this method the praseodymium accumulates in the most soluble portions. By fractionating the bromates the order is reversed, since lanthanum bromate is very much more soluble. At a temperature of 30° the latter compound crystallizes with great difficulty.

In the second case, where praseodymium and neodymium occur together, it is best to convert the double magnesium nitrates into the corresponding manganese compounds $2[M''(NO_3)_2] \cdot 3Mn(NO_3)_2 + 24H_2O$. In order to do this the magnesium double salts are dissolved in water, the solution acidified and the rare earths thrown down by oxalic acid. These oxalates are washed, dried and ignited to the oxides. The oxides are dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by manganese carbonate. Any peroxide remaining undissolved can be brought into solution by the addition of a few drops of dilute oxalic acid solution to the hot double nitrates. The manganese double salts are crystallized from nitric acid having a sp. gr. 1.3. This fractionation is carried on until the spectrum of neodymium disappears. A very concentrated solution of the nitrate should give no trace of the bands of the latter element even when observed through a thick layer.

The double nitrate (ammonium or manganese) is dissolved in water and precipitated with oxalic acid. This oxalate is free from all rare earth metals with perhaps the exception of traces of cerium. There are several methods for removing this element such as: (a) Boiling the almost neutral nitrate solution with potassium bromate and marble. Instead of marble a little precipitated calcium carbonate may be added occasionally as long as there is any effervescence. (b) Potassium permanganate and sodium carbonate. Since praseodymium is thrown down also to a slight extent the precipitates require working up again.

Praseodymium oxalate is shown at 11.

Separation of Nd.—The crude double magnesium neodymium nitrate forming (7) is the starting point for the preparation of pure neodymium salts. The mother liquors together with the most soluble crystals from the double manganese fractionation can also be used. Moreover, this last double salt can be used for the purification of neodymium with results equal to if not surpassing those of the magnesium salts. In the case of the double magnesium nitrates water is used as the solvent, which makes the process cheaper and more convenient to handle than nitric acid.

After more series of crystallizations have been carried out, the liquid assumes a beautiful bluish lilac color which is better seen when some of the liquid is diluted somewhat. The absorption bands in the blue stand out clearly. An excellent test of the purity of neodymium is found by observing the color of the oxide, which is blue when pure.

By crystallizing the bromates, the order of the solubilities is reversed; neodymium becomes the least soluble, while praseodymium passes into the mother liquors.

Pure neodymium material is found at (12) upon the diagram.

Sm and Eu Separation.—Fraction (8) contains not only samarium and europium but large quantities of gadolinium, yttrium, dysprosium and erbium earths. The double magnesium salts are crystallized from 30% nitric acid. The fractions rapidly change in their appearances, the least soluble showing the yellow tint due to samarium while the most soluble portions begin to crystallize badly owing to the quantities of yttrium earths present. At this point it is best to commence the addition of the isomorphous bismuth magnesium nitrate, which, as Urbain¹ has pointed out, places itself between samarium and europium. When working upon the large scale, the bismuth salt is crystallized through the mother liquors in portions of one kilogram at a time. This rapidly removes all europium from the yttrium earth nitrates. After crystallizing many times, the mother liquor, which shows a strong spectrum of dysprosium, holmium and erbium, is placed aside. The series is then allowed to expand to twenty or more fractions. Samarium is removed from the least soluble end, after a very large number of crystallizations, when it is considered certain that all europium has passed further along the series. As soon as the gadolinium fractions next to the samarium show a fine sharp absorption band in the blue—due to europium—nitric acid of about 50% is used as the solvent. By this time most of the samarium has been removed in a pure condition (13) and in addition nearly all the yttrium, dysprosium, erbium earths, together with quantities of gadolinium from the opposite end. Since the fractions now take up only a comparatively small space, it is best to transfer all to large casseroles, which can be covered with

¹ *Compt. rend.*, 138, 84.

watch glasses and so prevent a considerable amount of inconvenience and deliquescence. As the work proceeds, the europium band is observed to become stronger in the fractions between samarium and gadolinium. Later, the two bands in the green make their appearance. The fractions become smaller and smaller, since all mother liquors beyond one or two that give no europium spectrum have been removed. Only traces of samarium should be left by this time. Finally the samarium bands disappear and the remaining fractions consist almost entirely of bismuth magnesium nitrate. The fractions containing no gadolinium are mixed, diluted and all bismuth thrown out by means of hydrogen sulfide. The clear filtrate is next treated with oxalic acid, and the europium oxalate separated upon a Büchner funnel, washed and dried (14).

All the more soluble portions consisting of gadolinium together with varying amounts of yttrium, etc., form (15).

Separation of Gd.—The earths from fraction (15) are converted into oxalates. These are ignited to oxides and dissolved in nitric acid. The simple nitrates are then fractionated from strong nitric acid.¹ Gadolinium and terbium collect in the first crystals, dysprosium, holmium and yttrium come next, while yttrium, erbium, etc., accumulate in the mother liquors. These mother liquors are precipitated with oxalic acid, and the insoluble oxalates added to fraction (2). The intermediate nitrates consisting of dysprosium, holmium and yttrium form lot (17).

The least soluble nitrates comprising gadolinium and terbium (16) cannot be purified by the continued crystallization of the double magnesium nitrates since the oxide remains of a yellow color, even after many thousand operations. The crystallization of the simple nitrates effects a separation very slowly. Apparently the best method for obtaining a white gadolinia is that of the double nickel nitrate of the type $2\text{Gd}(\text{NO}_3)_3 \cdot 3\text{Ni}(\text{NO}_3)_2 + 24\text{H}_2\text{O}$.² This salt is crystallized from nitric acid of sp. gr. 1.3. Terbium collects in the more easily soluble crystals (24). The position of gadolinium is shown in the diagram at 18.

Separation of Crude Yt Earths.—Fraction 2, consisting of dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, and small amounts of gadolinium and terbium together with yttrium and scandium, is converted into the anhydrous sulfates by treating the oxalates with a slight excess of sulfuric acid and heating until all fumes of sulfuric acid cease to be evolved. The ignited sulfates are dissolved in cold water. The fairly strong solution is then gradually added to barium bromate covered with a layer of water and heated upon the steam bath.³ The mass is well stirred until decomposition is complete, i. e., when some

¹ Demarçay, *Compt. rend.*, 122, 728.

² Urbain, *Ibid.*, 140, No. 9.

³ James, *THIS JOURNAL*, 30, 132.

of the clear liquid gives no precipitate with barium bromate solution after diluting and boiling. It is necessary to dilute and boil, owing to the fact that a strong solution of the rare earth bromates causes a precipitate of barium bromate itself. The whole is next filtered, and the barium sulfate well washed with hot water. If the barium bromate is not in a very fine state of division, a large amount remains unattacked. The clear filtrate is evaporated until a drop removed upon the end of a glass rod nearly solidifies when stirred upon a watch glass. A little water is then sprayed upon the surface and the dish placed aside to crystallize. The mother liquor and the crystals are fractionally crystallized. The absorption spectrum soon shows that a rapid change is taking place. Samarium and gadolinium rapidly separate in the least soluble crystals (19) together with terbium. The next fractions are colored yellow and contain dysprosium, holmium and yttrium with very small quantities of terbium (20). The bromate that follows consists almost entirely of yttrium contaminated with very small quantities of dysprosium, holmium and erbium. Further along the series the bands of dysprosium and holmium disappear and the only impurity found is erbium (21). Practically the whole of the erbium is contained in the portions more soluble than yttrium (22). The erbium absorption is extremely intense and the solutions possess a beautiful rose red color. The mother liquors (23) are nearly colorless or possess only a very faint pink tint. The absorption spectrum shows only a trace of erbium together with a strong spectrum of thulium. This fraction consists almost entirely of ytterbium, lutecium and celtium.

Scandium occurs only in traces in the minerals usually worked up. Probably nearly all is lost during the oxalate precipitations, due to the fact that scandium oxalate is not entirely insoluble in water. The solubility is increased rapidly by free acid. During the fractional crystallization of salts, scandium tends to collect in the mother liquors. However, if the solutions become basic, it is likely to be found in the fractions further down the series. In the case of the bromates, the solutions gradually become basic owing to a slight decomposition. When this is the case, the mother liquors are free from scandium, while the erbium fractions contain small quantities. If dysprosium and holmium fractions are carefully examined, it will in all probability be found there as well. The various methods for the purification of scandium will be given towards the end of this paper.

The bromates forming (19) are converted into the simple nitrates, and fractionated from strong nitric acid similarly to the more soluble earths derived from the samarium-europium process. However, in this case, the least soluble goes to 24 and the more soluble to 17.

Separation of Tr.—Practically all the terbium concentrates in 21. In

addition to this element, there are also present gadolinium and dysprosium. Three methods have been used to separate this mixture: (a) Crystallization of the simple nitrates. (b) Fractional precipitation by ammonium hydroxide. (c) Crystallization of the ethylsulfates.

When the simple nitrates are used, it is best to add a quantity of bismuth nitrate, which is isomorphous with the rare nitrates and, as Urbain has shown, comes between gadolinium and dysprosium along with terbium. By fractionally crystallizing the nitrates from nitric acid for a few thousand times, it is found that bismuth nitrate accumulates in the middle fractions accompanied by terbium. Gadolinium is removed in the least soluble (26) portions, while dysprosium is removed in the mother liquors (27). The middle fractions are diluted and saturated with hydrogen sulfide. The bismuth sulfide is filtered off and the filtrate precipitated by means of oxalic acid. The terbium oxide obtained by igniting the oxalate (25) forms a black powder which in solution gives a characteristic absorption spectrum.

Fractional precipitation with very dilute ammonium hydroxide gradually concentrates terbium in the fractions slightly more basic than dysprosium.

When working with the ethylsulfates, terbium places itself between gadolinium and dysprosium.

Separation of Dy.—So far, the only really satisfactory method for the separation of pure dysprosium material is the crystallization of the ethylsulfates as proposed by Urbain. Fractions 17, 20 and 27 carry nearly all the dysprosium present in the original material. There are two methods by which the ethylsulfates may be prepared: (a) Action of the rare earth sulfate in solution upon barium ethylsulfate in a similar condition. (b) By mixing alcoholic solutions of the rare earth chlorides and sodium ethylsulfate.

When the writer endeavored to prepare the ethylsulfates by using the barium salt, the precipitates obtained often required days to filter. They were very difficult to wash, and, in addition, the barium sulfate, thrown down, entrained quantities of the rare dysprosium and holmium sulfates. It can readily be seen from this that the preparation of large quantities of material takes a very long time and also there is a loss of valuable material. These difficulties are all removed when we employ alcoholic solutions of the rare earth chloride and sodium ethylsulfate both hot and concentrated.

The fractions rich in dysprosium are precipitated with oxalic acid, the resulting oxalates filtered off and ignited to oxides. These oxides are then dissolved in hydrochloric acid. Small portions of oxides are then added until the solution becomes very slightly basic, after which the solution is evaporated to such a consistency that it would solidify upon

cooling. When it has cooled down considerably, but while still liquid, it is poured into a quantity of 95% alcohol. This last operation requires considerable care, if the mass is very hot. Because the salt is somewhat basic, the alcoholic solution is very turbid. This solution is now cleared by gradually adding concentrated hydrochloric acid drop by drop. Sodium ethylsulfate in alcohol, very hot and strong, is poured in and the whole well stirred. After heating for a while upon the water bath the crystallin precipitate of sodium chloride is filtered off, washed with hot alcohol and the filtrate set aside to crystallize. The mother liquor is poured off and the crystals well drained. The liquid and crystals are systematically fractionated for a very long time. The small quantity of terbium separates in the first few fractions, together with some dysprosium (28). Pure dysprosium (29) comes next, and these fractions are followed by dysprosium and holmium. The most soluble portions are found to contain holmium and yttrium (30).

Separation of Ho.—Holmium has never been obtained in a very pure form. Small quantities may be freed from dysprosium, but then again the fractions so obtained are very rich in yttrium and carry a little erbium. The fusion of the nitrates is as yet the best method for separating yttrium from holmium. However, this method calls for more material than is usually obtained. Probably two or three years may elapse before this element is obtained in the form of a pure compound. Fraction 30 upon the diagram must be converted into the nitrate and fractionated as described under yttrium. This should eventually give a pure basic holmium nitrate (31) while yttrium nitrate and some holmium nitrate (32) will remain as the more stable portion.

Separation of Yt.—The best sources for yttrium are found in fractions 21 and 35, *i. e.*, if the latter has been obtained.

Many methods have been described for the purification of yttrium such as: The chromate method; the decomposition of the nitrate by fusion; the action of magnesium oxide upon a concentrated boiling solution of the nitrate; etc.

The chromate method is very useful, if terbium is present as an impurity. However, under usual conditions (when bromates or ethylsulfates have been used) it is absent. Muthmann and Böhm's chromate method, one of the best, is as follows:

The oxides are dissolved in chromic acid solution, 40 grams R_2O_3 are contained in each liter. The liquid is then treated with potassium chromate solution until it becomes cloudy. It is placed in a retort, heated to boiling, and rapidly stirred with a current of steam. Another tube passing through the cork carries a stopcock by means of which the potassium chromate solution can be added and controlled. Six fractions are usually taken. Fractions I and II are obtained by employing 10% po-

tassium chromate solution. To get the remaining fractions, potassium chromate of 5% strength is used. By regulating the burner underneath the retort, the volume can be kept constant. This method is excellent when one is working upon a small scale. The writer finds that a neutral earth nitrate solution, to which potassium dichromate has been added, works as well as the chromate solution.

When there are large quantities of yttrium material to be purified the old method of fusing the nitrates is undoubtedly the best. If terbium is present as an impurity, a pure white yttrium oxide cannot be obtained. In order to carry out this method the oxides are dissolved in nitric acid, the solution evaporated and the nitrates fused until a portion has decomposed. When working on a large scale, porcelain dishes are used, while casseroles are found very convenient for smaller amounts. During the decomposition, the evolution of red fumes is allowed to proceed until the surface assumes a glazed appearance. This point is easily ascertained by experience. The decomposition should never be allowed to advance so that the mass becomes of a thick creamy nature. The best method for obtaining a solution of the melt is to pour the fused mass into a sufficient quantity of cold water. Great care, however, is required and stirring usually aids the operation very much. A large amount of cold water must be avoided, since it is desired that the solution should be concentrated after about five minutes' boiling. As the fused nitrate is gradually added to the water, the temperature rapidly rises and the whole suddenly begins to boil violently. When the dish, which contained the melted salt, has cooled sufficiently, a little water is added and the whole heated until the glassy mass has disintegrated, after which it is added to the main bulk. The latter is then boiled for five minutes and set aside to cool.

Under the best conditions the entire mass goes into solution; especially is this true of the yttrium end of the series. Upon cooling it will be found that the basic nitrate separates in a crystalline form. At the opposite end, the least basic portion of the fractions, there always remains an insoluble basic nitrate, unless the decomposition is stopped at an earlier stage, *i. e.*, when there is a copious evolution of red fumes.

In case a precipitate remains, it is highly important that it be well agitated by thoroughly boiling. After cooling, the precipitate (fraction B) is filtered off, redissolved in nitric acid and again fused. The filtrate (fraction A) is also boiled down and fused. This second series gives two filtrates and two precipitates. The filtrate from fraction B is mixed with the precipitate from fraction A with the result that the second series contains three fractions, etc.

Pure yttrium nitrate, which is eventually obtained, forms lot 33 upon the diagram while the less basic portion forms 34.

Separation of Er.—Fractions 34 and 22 contain practically the whole

of the erbium found in the original mineral. It contains a considerable amount of yttrium with perhaps traces of scandium, thulium and holmium. Yttrium is best separated by fractionally decomposing the nitrate by fusion. Since erbium nitrate decomposes easily, the temperature is not raised quite so high as in the case of nearly pure yttrium. The least basic portion, obtained after a large number of series, consists of erbium basic nitrate (36). The yttrium concentrates in more basic fractions, which, when united, form 35. The best method for removing scandium is to crystallize the nitrates from nitric acid (fairly strong). Holmium and thulium are separated, if still found contaminating the material, by converting back to the bromate and employing fractional crystallization from water. This last method also causes yttrium to pass into the less soluble crystals.

According to work carried out by the author, erbium is not nearly so common as many are led to believe. During concentration, the material rapidly becomes less, the erbium solutions become more rose colored and the absorption spectrum appears very intense.

Separation of Tm.—For the preparation of pure thulium material the most soluble fractions, obtained during the original bromate crystallizations, are used. These contain thulium, ytterbium, lutecium and celtium with traces of erbium. The solution is nearly colorless. It shows the absorption bands of thulium and mere traces of those of erbium. Usually, however, the greater portion consists of the ytterbium metals. The fractionation of the bromates is carried on in a room which has a temperature of about 16°. Higher temperatures are inconvenient, owing to the formation of very concentrated solutions. Casseroles form the best containers, and the concentration should be such that the greater portion separates in the solid condition upon cooling. From the fact that supersaturated solutions tend to form with extreme ease, the crystallization must necessarily be started by a tiny crystal.

During the first few series, erbium rapidly separates in the least soluble portion, after which, the other fractions become colored greenish. As soon as the mother liquors fail to give any thulium absorption bands, when examined in a saturated solution of about 10 cm., they are placed aside for the preparation of ytterbium, etc. Thulium is found to collect in the fractions between erbium and ytterbium. The solutions become colored a faint bluish green and show a very intense absorption spectrum consisting of three bands. If very great care is taken, dilute alcohol can be used as solvent for a short time—best towards the end of the work. However, it soon shows signs of being attacked by the bromate.

Thulium is very rare, and in order to obtain a few grams of the oxide in a pure condition, one must commence with large quantities of suitable mineral.

Yb, and Lu, Ct.—Ytterbium, lutecium and celtium are contained in the mother liquors from the purification of thulium (38). They can be fractionated by means of the bromates, if the solution be not allowed to become basic. One must deal with large amounts owing to their great solubilities. Urbain recommends the use of the nitrates from nitric acid.

Celtium is said to occur in gadolinite, from the crude earths of which it can be separated by repeatedly crystallizing the simple nitrates from nitric acid. It separates in the mother liquor, being more soluble than lutecium.

Scandium.—Scandium occurs in few minerals to any extent, such as wiikite from Lake Ladoga, Finland,¹ also in orthite from the same locality,² also in residues from the working up of certain tungsten minerals. This element is easily detected by means of its spectrum, as Crookes has pointed out, and, when found to occur in any fractions or in minerals in quantity, can be separated by methods of R. J. Meyer. (a) The hydrochloric acid solution is precipitated with sodium silicofluoride.³ (b) Scandium can also be separated by sodium thiosulfate. Meyer says the separation is almost quantitative; no trace of scandium remains in the filtrate; the precipitate contains thorium (if present) and only very small amounts of the yttrium earths, which can be removed by repeated precipitation with thiosulfate. This method is better than the sodium silicofluoride.

(c) Separation of thorium and scandium by means of sodium carbonate: The concentrated chloride solution is poured into a solution of sodium carbonate containing 20% of anhydrous carbonate. One liter of sodium carbonate solution is used for every 10 g. of scandium oxide. The scandium dissolves entirely on stirring and warming. It is then boiled rapidly for half an hour, when the double carbonate is precipitated as a powder. The volume of the solution should be kept constant during the boiling. After the crystallin powder has settled, the liquid is poured off, and the precipitate washed by boiling with 20% sodium carbonate solution for 15 minutes—this is repeated three times. The double carbonate is dissolved in two liters of cold water; four hours and constant stirring are required for this purpose. The liquid is then filtered, acidified with hydrochloric acid and the hydroxide thrown down by ammonium hydroxide while boiling. The scandium hydroxide is filtered off and well washed with boiling water until free from alkali. If necessary, the operation is performed again. Finally the chloride solution is precipitated with oxalic acid.

DURHAM, NEW HAMPSHIRE,
March 18, 1912:

¹ Crookes, *Proc. Roy. Soc.*, 80, (A), 516.

² R. J. Meyer, *Sitzungsber. K. Akad. Wiss.*, Berlin, 1911, 379.

³ *Z. anorg. Chem.*, 67, 398.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

THE QUANTITATIVE DETERMINATION OF YTTRIUM.

BY C. F. WHITTEMORE AND C. JAMES.

Received March 29, 1912.

Having encountered difficulties in the determination of yttrium in the presence of sodium, the authors made a systematic study of the quantitative determination of yttrium in the presence of this and certain other elements.

A neutral solution of yttrium chloride was first prepared and carefully standardized by precipitation with oxalic acid. Then the yttrium in 25 cc. portions of this solution was precipitated with various reagents in the presence of other elements.

In the Presence of Sodium.—For the purpose of studying the separation from sodium, 10 cc. of a saturated solution of sodium sulfate were added to each 25 cc. sample of the standard yttrium chloride solution. Sodium hydroxide, the first reagent employed, gave the following results:

No. of cc. standard YCl ₃ solution.	No. of cc. of sat- urated solution of Na ₂ SO ₄ present.	Y ₂ O ₃ found. Gram.	Y ₂ O ₃ in standard. Gram.
25	10	0.1642
25	10	0.1647
25	10	0.1640
25	10	0.1647
25	10	0.1638
25	10	0.1640
		—————	—————
		Average, 0.1642	0.1575

Since these figures were considerably too high, 5 *N* ammonium hydroxide was tried but with equally unsatisfactory results.

Oxalic acid gave exceedingly high results due to the carrying down of sodium.

The next precipitants used were the ammonium salts of several organic compounds.

Ammonium anisate formed a precipitate which gave low results owing to its slight solubility.

Yttrium palmitate was investigated but was found unsatisfactory and no determination was made.

Ammonium phthalate and ammonium fumarate formed no precipitates with yttrium chloride in dilute solution, probably on account of the formation of soluble double compounds.

Ammonium benzoate precipitated yttrium from the neutral solution at first, but the compound dissolved in an excess of the reagent.

The next reagent, ammonium sebacate, gave a perfectly quantitative separation, and the precipitated yttrium sebacate was found to be com-

paratively easy to filter off and wash. The average of several determinations showed a good agreement with the standard:

No. of cc. of standard YCl_3 solution.	No. of cc. of saturated solution Na_2SO_4 present.	Y_2O_3 found. Gram.	Y_2O_3 in standard. Gram.
25	10	0.1582
25	10	0.1573
25	10	0.1581
25	10	0.1579
		Average, 0.1578	0.1575

In the Presence of Potassium.—Having eliminated the difficulty of the separation of yttrium from sodium, the separation from potassium was next taken under consideration. Ammonium hydroxide and ammonium sebacate were tried without success. Finally a double precipitation, as the sebacate, proved satisfactory. The following data were obtained.

AMMONIUM HYDROXIDE.

No. of cc. of standard YCl_3 solution.	No. of cc. of saturated solution of K_2SO_4 present.	Y_2O_3 found. Gram.	Y_2O_3 in standard. Gram.
25	5	0.1629
25	5	0.1625
		Average, 0.1627	0.1575

AMMONIUM SEBACATE.

25	5	0.1592
25	5	0.1599
25	5	0.1590
25	5	0.1596
		Average, 0.1594	0.1575

AMMONIUM SEBACATE.

Double Precipitation.

25	5	0.1536
25	5	0.1542
		Average, 0.1539	0.1537

After finding a satisfactory separation from sodium and potassium it seemed advisable to study the separation from iron, aluminium, lithium and magnesium. As the result of several trials, it was found that yttrium could be quantitatively separated as the oxalate in the presence of ammonium chloride.

In the Presence of Iron.—10 cc. of a 10% ferric chloride solution were added to 25 cc. of the standard yttrium chloride solution and the whole diluted to approximately 100 cc. After heating to boiling, the yttrium was precipitated by means of oxalic acid. This oxalate was first slightly reddish brown but became white on standing. The ignited oxide, how-

ever, was slightly colored. Other determinations were made in which the oxalate was precipitated from a cold solution with ammonium chloride present. In this case, a white oxide was obtained. The average of these determinations agreed well with the standard:

Average Y_2O_3 in presence of $FeCl_3$, 0.1536 gm.; Y_2O_3 in standard, 0.1537 gm.

In the Presence of Aluminium.—In order to study the determination of yttrium in the presence of aluminium, 10 cc. of a 10% aluminium chloride solution were added to the 25 cc. sample of the standard solution. Yttrium oxalate was precipitated from the cold solution in the presence of ammonium chloride. The result of this determination was also in close agreement with the standard:

Average Y_2O_3 in presence of $AlCl_3$, 0.1539 gm.; Y_2O_3 in standard, 0.1537 gm.

In the Presence of Lithium.—To the 25 cc. of the standard solution of yttrium chloride, 10 cc. of a 10% lithium chloride solution were added. Yttrium was precipitated as in the previous case and with equally satisfactory results:

Average Y_2O_3 in the presence of $LiCl$, 0.1536 gm.; Y_2O_3 in standard 0.1537 gm.

In the Presence of Magnesium.—Yttrium oxalate was precipitated from 25 cc. samples of the standard yttrium chloride solution to which 10 cc. of a 10% magnesium chloride solution had been added. As in the preceding cases, there was a complete separation:

Average Y_2O_3 in presence of $MgCl_2$, 0.1537 gm.; Y_2O_3 in standard, 0.1537 gm.

Summary.

1. Ammonium sebacate affords a quantitative separation of yttrium from sodium.
2. A double precipitation with the same reagent gives a complete separation from potassium.
3. Oxalic acid in the presence of ammonium chloride effects a perfectly satisfactory separation from iron, aluminium, lithium and magnesium.

DURHAM, NEW HAMPSHIRE.

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF HARVARD MEDICAL SCHOOL.]
IS IONIZATION, AS INDICATED BY CONDUCTIVITY, A NECESSARY PREREQUISITE FOR THE COMBINATION OF ACIDS WITH BASES?

BY OTTO FOLIN AND FRED F. FLANDERS.

Received March 11, 1912.

Sometime ago a method was described by Folin and Wentworth, based on the titration of acids by means of sodium ethylate, using as solvents

organic liquids such as chloroform, benzene, toluene, or carbon tetrachloride, and was found satisfactory for the determination of fatty acids.¹ Since that time a practical method for the determination of benzoic acid has been worked out,² and more recently a method for the estimation of hippuric acid in urin, based on the same principle.³

Viewed from the standpoint of the electrolytic dissociation theory, the conditions of these titrations are unusual, and apparently not entirely in accord with the current views.

The reaction between an acid and an alkali is to be regarded as a typical ionic reaction. Walker⁴ states "acidity is, on the theory of electrolytic dissociation, attributed to the presence of hydrion and alkalinity to the presence of hydroxidion in the solution." Therefore the reaction between an acid and an alkali, in its last analysis, must be the reaction between hydrion and hydroxidion.

In organic solvents, however, reactions cannot so easily be regarded as ion reactions. According to Ostwald⁵ substances are not ionized in solvents of the character of benzene. He says, "In order therefore to separate a substance from its solution in water by ether, benzene, or any such liquid, it must be brought into a condition in which it is neither an ion itself, nor a constituent of one." "It is only the non-ionized portion which is affected by the process of extraction."

From this point of view then, an acid could only be present in solution in benzene in the unionized state. This idea is confirmed, in so far at least as benzoic acid in benzene is concerned, by Walker⁶ who gives the molecular weight of benzoic acid, determined by the freezing-point method in benzene, as 223-236, showing that it corresponds nearly to double molecules. Many investigators⁷ have shown that substances are ionized to a far less degree in alcohol than in water. According to Kablukoff⁸ the ionization decreases as the molecular weight of the alcohol increases. The same investigator finds that even hydrochloric acid is only very feebly ionized in such solvents as benzene, toluene and xylene.⁹

Furthermore, that there is a certain parallelism between ionization and

¹ Folin and Wentworth, *J. Biol. Chem.*, 7, 421 (1910).

² Folin and Flanders, *J. Am. Chem. Soc.*, 33, 161 (1911).

³ Folin and Flanders, *J. Biol. Chem.*, 11, 257 (1912).

⁴ "Introduction to Phys. Chem.," p. 315, 5th ed.

⁵ Ostwald, "Sci. Foundations of Anal. Chem.," 3d Eng. ed., p. 94. See also p. 56 for similar statements.

⁶ Walker, "Elements of Phys. Chem.," 5th ed., p. 205.

⁷ Fitzpatrick, *Phil. Mag.*, 24, 378 (1887). Hartwig, *Wied. Ann.*, 33, 58 (1888); 43, 838 (1891). Völlmer, *Ibid.*, 52, 328 (1894). Kawalki, *Ibid.*, 52, 324 (1894). Schall, *Z. physik. Chem.*, 14, 701 (1894). Kablukoff, *Ibid.*, 4, 429 (1898). Jones, *Ibid.*, 31, 133 (1899).

⁸ *Z. physik. Chem.*, 4, 432 (1889).

⁹ *Ibid.*, 4, 429 (1889).

chemical reactivity on the one hand and chemical reactivity and conductivity on the other, seems to be a fundamental concept of the theory of electrolytic dissociation. Jones¹ says "Molecules as such have little or no chemical affinity;" and "We have already reached a point where we can say that nearly all, if not all chemical reactions are due to ions, molecules as such not entering into chemical action."

Ostwald² outlines a certain experiment, "To show the parallelism between conducting power and capability of chemical reaction."

The failure of dry hydrogen sulfide³ to precipitate mercuric chloride in absolute alcohol has been cited as due to lack of ionization.⁴ From these various expressions, one is led to the conclusion that a solution of a substance, to possess chemical reactivity, must be ionized, and that this ionization would be disclosed by its conductivity. Or conversely, a substance which did not exhibit some degree of conductivity would appear to be non-ionized and hence would ordinarily not be expected to possess chemical reactivity. Kahlenberg, however, has never accepted the electrolytic dissociation theory and from among his many ingenious experiments, made to show that it does not hold for reactions in organic solvents, may be mentioned the reaction of dry hydrogen chloride on dry copper oleate in benzene solution.⁵

Our experimental evidence proves that all classes of acids may be titrated by sodium ethylate, in organic solvents. The only limitation seems to be that of solubility of the acid in the solvent employed. Acids which were not readily soluble in chloroform were first dissolved in 10 cc. of absolute alcohol, diluting to 100 cc. with chloroform. Oxalic, succinic, malic, citric and tartaric acids were treated in this manner and found to give sharp end points. Hydrochloric, acetic, propionic, caproic, cinnamic, lactic, salicylic, benzoic and picric acids were dissolved in chloroform alone. The end points were excellent. Even picric acid yielded quantitative results. Particularly, the very weak acids which cannot be titrated at all in aqueous solution on account of hydrolysis, are found to yield excellent results in organic solvents. This point has been tested on stearic, palmitic and oleic acids, and even on hydrogen sulphide. The latter, dissolved in chloroform, titrates with a fairly sharp end point when phenolphthalein is employed as indicator. Carbon dioxide could

¹ "Elements of Phys. Chem.," p. 440, 4th ed.

² "Sci. Foundations of Anal. Chem.," 3d Eng. ed., p. 236.

³ Jones, "Elements Phys. Chem.," p. 439.

⁴ Purely as a matter of interest, we have found that mercuric chloride dissolved in equal parts of absolute alcohol and benzene can be titrated with sodium ethylate giving a fair end point with phenolphthalein. The titration appears to be nearly quantitative.

⁵ Kahlenberg, *J. Physic. Chem.*, 6, 1 (1902). See also Stieglitz, "Qual. Anal.," Vol. 1 (1911), pp. 72 to 87, for a most interesting discussion of this phase of the subject.

not be titrated either in chloroform or in benzene. The reason for this is obvious, carbon dioxide in the absence of water not being an acid.

In view of the apparent discrepancy between our own observations and the accepted teachings it seemed to us well worth while to determine the conductivity of some of our solutions. The results obtained have, however, not cleared up this discrepancy, as shown by the specific conductivities recorded below:

Solution.		Specific conductivity at 18°.
0.1 N sodium ethylate.....	(Prepared from sodium and absolute alcohol)	1.4×10^{-3}
0.05 N sodium ethylate.....	(0.1 N sodium ethylate diluted with an equal volume of benzene)	1.6×10^{-4}
0.1 N benzoic acid.....	In pure benzene	Too small to measure
0.05 N benzoic acid.....	(0.1 N benzoic acid in benzene diluted with an equal volume absolute alcohol)	8.6×10^{-7}
Sodium benzoate.....	(Saturated soln. in equal parts absolute alcohol and benzene)	2.8×10^{-3}

As was to be expected, the conductivity of the benzoic acid in benzene was immeasurably small.

The benzoic acid solution, whether in a mixture of alcohol and benzene or benzene alone, could be titrated with a perfectly sharp end point, either by the sodium ethylate or the same diluted with an equal volume of benzene. The presence of benzene considerably decreases the conductivity of the solutions, but not the reactivity, as the titrations were as sharp as when the larger proportions of alcohol were used. The sodium benzoate is not very soluble in the mixed solvent, and is partially precipitated toward the end of the titration.

In order to avoid this difficulty, a solution of oleic acid was prepared for study. Sodium amylate was used as the alkali, as, according to Kablukoff,¹ it might be expected to have much less conductivity than the ethylate. The following table gives the conductivities of the solutions employed:

Solution.		Specific conductivity at 18°.
0.1 N sodium amylate.....	In pure amyl alcohol	2.2×10^{-5}
0.05 N sodium amylate.....	(A new soln. of amylate in equal parts amyl alcohol and benzene)	3.3×10^{-7}
0.1 N oleic acid.....	In pure benzene	Too small to measure
0.025 N sodium oleate.....	(In equal parts amyl alcohol and benzene)	2.5×10^{-7}
0.1 N benzoic acid.....	In pure amyl alcohol	3.8×10^{-7}
Pure amyl alcohol.....	4.5×10^{-7}

¹ *Loc. cit.*

The amyl alcohol itself had some conductivity, as is shown by the figure on the pure solvent. It, as well as the benzene, had been treated with sodium and distilled.

Titration were made with the 0.05 *N* amylate in mixed amyl alcohol and benzene, against the oleic acid in pure benzene, and also by adding an equal volume of amyl alcohol before titrating. The end points were sharp and satisfactory. The 0.025 *N* sodium oleate was prepared by titrating a measured amount of oleic acid in benzene, to which had been added an equal volume of amyl alcohol, with the 0.05 *N* amylate in 50% benzene solution.

The table shows one interesting feature. With the exception of the first, the conductivities of the solutions appear to be almost independent of the dissolved substance; that is, they are of about the same order as the amyl alcohol itself and are possibly due to it in each case. The first solution of sodium amylate in alcohol had been prepared from alcohol which had not been treated with sodium and distilled, and its greater conductivity is probably due to this fact. Titrations were made with both this solution and that from purified alcohol mixed with benzene. No difference could be observed in speed of titration or sharpness of the end point.

Other indicators than phenolphthalein were also tried, with the oleic acid and sodium amylate, both made up in a mixture of equal parts of amyl alcohol and benzene. Phenolphthalein, thymolphthalein, rosolic acid, alizarin, hematoxylin and alizarin red gave results as regards sharpness of end point, about in the order named. Any one of the first three named might be used with a fair degree of success. Phenolphthalein is, however, the most satisfactory. Other indicators, congo red, methyl orange, eosin, fluorescein, tropaeolin oo, and dimethylaminoazobenzene were tried. None of these gave the acid reaction with oleic acid. From this it appears that the distinction between mineral and other acids holds here as in aqueous solutions. A trace of mineral acid shaken with the solution gave the acid reaction with all the indicators.

The conductivity measurements recorded in this paper were made with the Ostwald cell, with plates set about 0.5 cm. apart. Unusual accuracy is not claimed for the measurements. The resistance of the solutions is very high, and accurate measurements would require apparatus especially suited to this class of work. We are not prepared to assert that our solutions were absolutely free from water, in the sense used in physical chemistry, nor to deny that the results which we obtain on titrating weak acids in organic solvents, can be explained on the basis of the enormous speed of a few ions which may be present without appreciably affecting the conductivity of the solutions.¹ It is of course a

¹ Haber, *Z. Elektrochem.*, 10, 433, 473 (1904).

fact that we have always had some alcohol present in our titrations, as carrier of the alcoholate, and even amyl alcohol has some dissociating power. Curiously enough, however, the addition of alcohol in larger amounts makes the end point of the titrations less sharp than when the amount of alcohol is kept at a minimum. We would emphasize that our titrations have been made with solutions of acid and alkali which have almost no conductivity, that the resulting salt solutions also have practically no conductivity, that the reaction is instant and that the action of the indicator does not differ materially from that observed in aqueous solutions.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 82.]

THE DISSOCIATION PRESSURES OF SODIUM AND POTASSIUM HYDRIDES.

By FREDERICK G. KEYES.

Received March 23, 1912.

I. Review of Previous Investigations.

Gay-Lussac and Thénard¹ were the first to observe that metallic sodium and potassium absorb hydrogen. In the case of sodium no quantitative results were obtained. They observed, however, in the case of potassium, that one equivalent of the metal absorbed one-quarter of an equivalent of hydrogen.

Troost and Hautefeuille² studied the reaction and measured the equilibrium pressure of hydrogen over both the metals. They also attempted to determine the composition of the hydrides. The analysis was made by saturating a definite weight of metal and subsequently pumping out and measuring the hydrogen gas. No details of the experiments are given, but the formulas Na_3H and K_3H are assigned. Equilibrium measurements for both hydrides were made from 330° to 430° . The values will be presented below.

Henri Moissan³ prepared both hydrides by heating the metals in a current of hydrogen gas. The excess of metal was then extracted from the product by means of liquid ammonia. The analysis of the hydrides thus obtained was made by decomposing the compounds with water and measuring the volume of gas evolved. The data gave the formulas NaH and KH . Moissan studied various properties of the hydrides. He found that they were insoluble in organic solvents, and that they reacted with carbon dioxide to form formates. The dissociation pressures were not measured.

¹ *Recherches physico-chimiques*, 1, 176.

² *Compt. rend.*, 78, 807 (1874).

³ *Ibid.*, 134, 71 (1902).

2. The Experimental Method.

The apparatus used to study the dissociation of the hydrides is represented in Fig. 1. The method followed was to distil the metals into the reaction tubes and then to connect them with the manometers without permitting contact with the air. The manometers being exhausted, hydrogen was admitted and the reaction tubes were heated, by means of a resistance furnace, to the desired temperature.

The metals used were taken from the same stock as was employed in the electrode potential measurements of Lewis and Kraus¹ and Lewis and Keyes.²

The hydrogen was prepared *in vacuo* by the action of air free distilled water on 4% sodium amalgam. The apparatus for this purpose is represented by I (Fig. 1). The amalgam was placed in I and distilled water

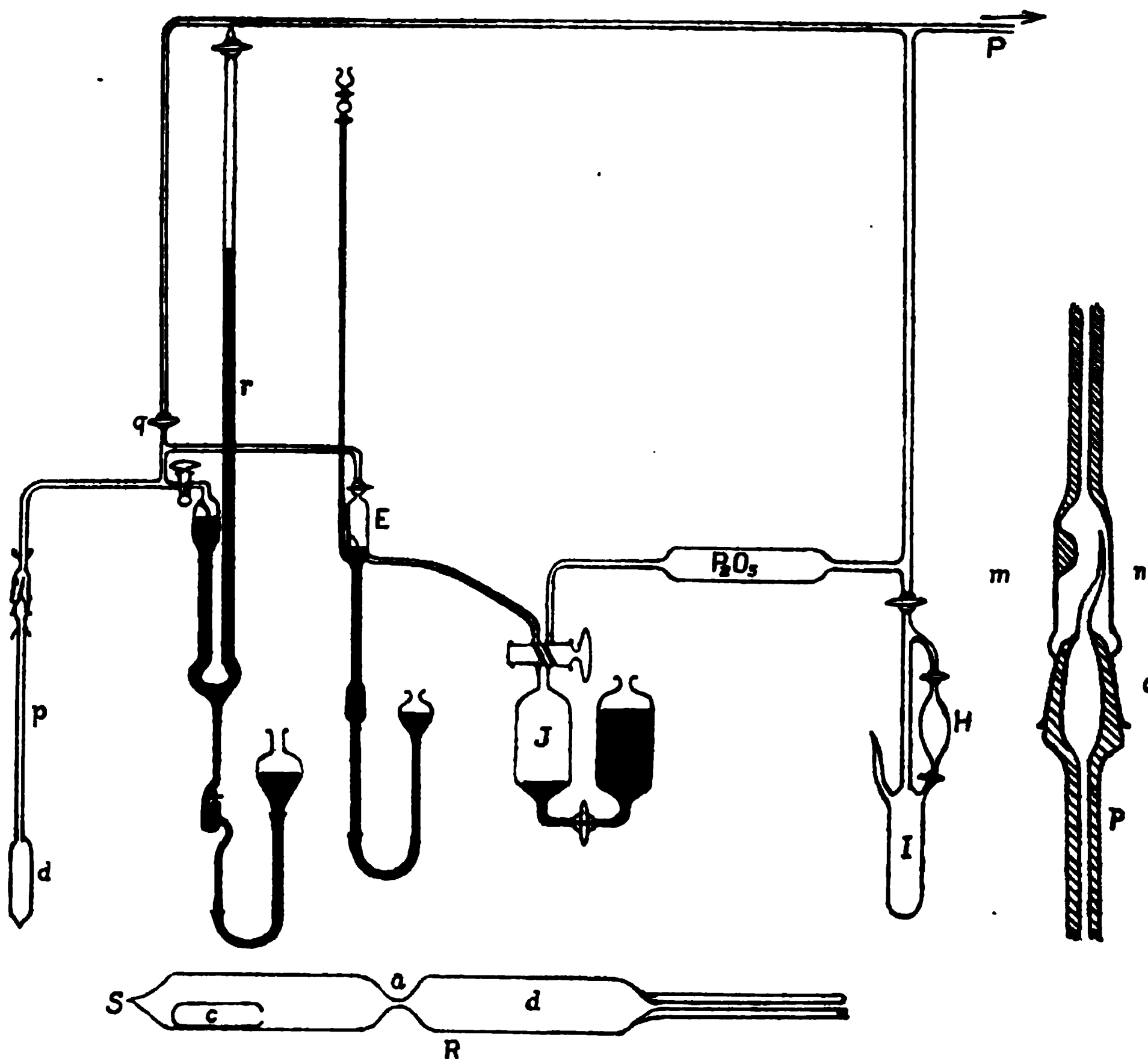


Fig. 1.

¹ THIS JOURNAL, 32, 1459 (1910).

² *Ibid.*, 34, 119 (1912).

in H. The apparatus, including the part J, was thoroughly exhausted through P. The stopcock at the upper end of the water chamber H was opened during the exhaustion for the purpose of boiling the water, thus freeing it completely from dissolved air. After exhaustion, a few drops of water were admitted to the amalgam and the whole apparatus re-exhausted. The water was then run onto the amalgam, and the evolved hydrogen, after being dried by means of the phosphorus pent-oxide tube shown in the figure, was collected in the reservoir J.

The method of preparing the reaction tubes *d* was as follows: A small portion of metal was placed in the capsule *c*. The latter was then introduced into the reaction tube R and the end of the reaction tube sealed off at S. The capillary portion of the reaction tube was joined to the ground connection *p*. The tip of the latter was then sealed to the pump, and the whole reaction tube completely exhausted. By means of a cylindrical resistance heater which slipped over the tube R the metal could be distilled into the part of the tube marked *d*. The portion of the reaction tube containing the capsule could then be sealed off at *a* and the tip *n* sealed from the pump. Connection was then made with the manometers *r* by means of the ground glass piece *m*. After exhausting the manometer connections, the reaction tube *n* was rotated in the ground glass joint until the tip *n* pressed against the glass projection inside *m*, thus breaking off the tip and affording communication with the inside of the reaction tube. By this device the clean distilled metal could be introduced without contact with the air. Hydrogen was now admitted from the reservoir J, and the temperature of the furnace having been adjusted, the equilibrium pressures could be read off directly on the manometer *r*.

The furnace used was constructed of a 35 cm. length of iron pipe having an internal diameter of 15 cm. The pipe was covered with asbestos cloth and mica, and was wound with suitable resistance wire. A fan was introduced from the bottom of the furnace to provide vigorous stirring. As has been pointed out before, vigorous stirring is essential if a uniform temperature is desired. Temperatures were measured by means of a copper-constantan thermoelement. The temperature-electromotive force curve for the couple was obtained from the boiling points of water, naphthalene, benzophenone, and sulphur. The values for the boiling points under atmospheric pressure, together with the electromotive force values, are given in the following table:

	Boiling-point.	E. M. F. in millivolts.
Water.....	100.0	3.150
Naphthalene ¹	218.0	8.830
Benzophenone ¹	306.0	13.550
Sulphur.....	444.7	21.57

¹ *Bull. Bureau of Standards*, 7, 8 (1911).

The attempt was made to study the rate of the reaction at different temperatures. The measuring chamber E was used to introduce a measured volume of hydrogen; and from this and the known volume of the reaction tube the initial pressure could be computed. The rate was not proportional to the hydrogen pressure, owing probably to surface effects in the reaction bulb. The rate¹ of absorption of hydrogen, however, is approximately sixteen times as rapid at 300° as at 200°. Above 300° the rate of absorption of hydrogen was so rapid that accurate readings could not be obtained on the manometer.

Some difficulty was experienced above 375°–400°, owing to the action of the metal on the glass. The glass walls of the reaction tube were of course thoroughly heated before distilling in the metal. This precaution seemed to lessen the action very materially. In the case of sodium, the action was much more marked than in the case of potassium. The result of this action on the glass seemed to be the production of a gaseous product, since on lowering the temperature—say to 300°—the observed pressure was greatly in excess of the equilibrium pressure. On the other hand, in the case of experiments where a temperature of 380°–400° was not exceeded, the equilibrium pressures at the lower temperatures could be produced exactly. In fact, the equilibrium pressures were obtained with both increasing and decreasing temperature in every experiment. On account of the difficulty described above, no measurements were made much above 400°.

3. The Vapor Pressures of Liquid Sodium and Potassium.

The equilibrium pressure determined by the method described above is the sum of the partial pressures of the hydrogen in equilibrium with the metal, the vapor pressure of the solid metal hydride, and that of the metal. The equilibrium pressure of the hydrogen alone is needed to determine the constants in the equation which is to represent the results. The vapor pressure of the solid metal hydride was neglected. The vapor pressures of the metals have been measured only in the case of sodium. Jewett² determined the vapor density of metallic sodium, and from the data obtained he computed the vapor pressure at the corresponding temperatures. Gebhardt³ measured directly the vapor pressure of this metal between 380° and 570° in a glass apparatus. The two sets of data do not agree even approximately—Jewett giving 10.72 mm. at 410° and Gebhardt 1.7 mm. at the same temperature. In view of the action of the metal on glass referred to above, it is probable that even Gebhardt's

¹ In 2¼ min. at 300° the pressure dropped from 575 mm. to 501 mm., while at 215° the pressure fell from 477.5 mm. to 418 mm. in 39 min.

² *Phil. Mag.*, 4, 546 (1902).

³ *Ber. physik. Ges.*, 3, 184 (1905).

values are much too high. That there are in reality serious errors in Gebhardt's data is shown by the fact that they give values for the heat of evaporation of the metal which increases enormously with increasing temperature, whereas they should decrease.

A more reliable estimate of the vapor pressure may be obtained by means of the following computation based upon the vapor pressure equation of Clausius and on Trouton's rule, which states that the ratio of the molal heat of vaporization to the boiling point on the absolute scale is constant. Mercury has been found to give the value 22 for Trouton's constant. Assuming that this constant has the same value for sodium and potassium, and taking the boiling points of these metals as 878° and 758° , we obtain 25,322 cal. and 22,678 cal., respectively, for the atomic heats of evaporation (L). With the aid of these data, and of the difference (ΔC_p) of the atomic heat capacities of the liquid metal (as given by Bernini¹) and of the monatomic vapor (as calculated from the kinetic theory), we may substitute numerical values in the following thermodynamic equation expressing the change of the vapor pressure p with the temperature T :

$$\log p = \int \frac{L_0 + (\Delta C_p)T}{RT^2} dT + \text{const.}$$

We thus obtain the equations:

$$\text{For Na: } \log_{10} p = -\frac{6200}{T} - 1.35 \log_{10} T + 12.40.$$

$$\text{For K: } \log_{10} p = -\frac{6000}{T} - 0.40 \log_{10} T - 0.0008T + 10.73.$$

These equations give for the vapor pressure of sodium at 400° , 0.24 mm., and for that of potassium, 1.4 mm. The magnitude of the vapor-pressure of the metals themselves may therefore be neglected, in comparison with the dissociation pressure of the hydrides.

4. The Equilibrium Pressures of Sodium Hydride.

A large number of reaction tubes were prepared in the manner already described. No effort was made to adjust the temperature for fixed intervals or at any particular point, but measurements were made at various temperatures between about 250° and 400° . The equilibrium pressures within this interval were obtainable for either rising or falling temperatures. The separate observations are given in Table I. The pressures are expressed in millimeters of mercury.

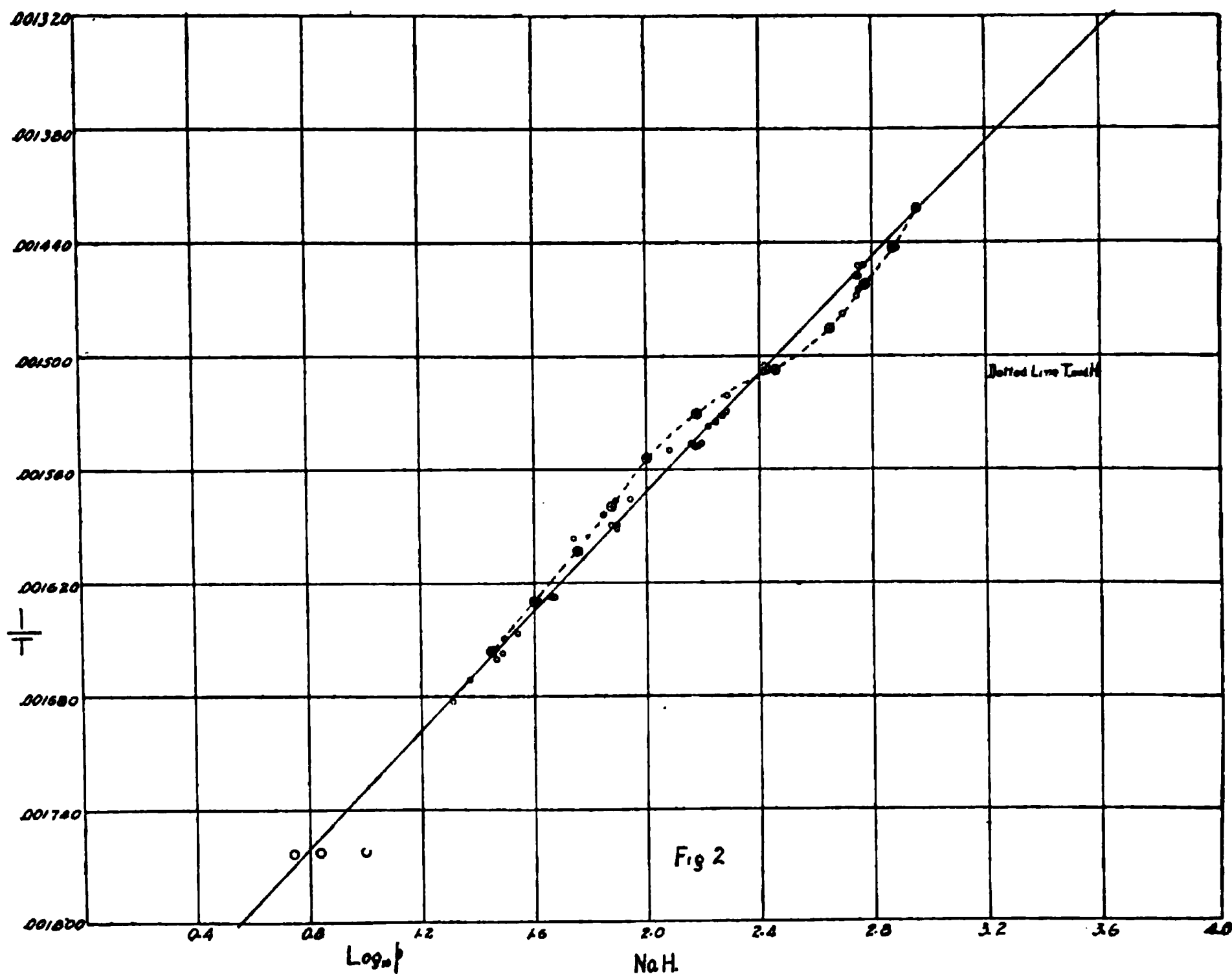
These data were combined by plotting the logarithm of the pressure in millimeters against the reciprocal of the absolute temperature. A

¹ *Physik. Z.*, 7, 168 (1906).

TABLE I.—OBSERVED VALUES OF THE VAPOR PRESSURE OF SODIUM HYDRIDE.

t	p	t	p	t	p	t	p
267.0°	1.5	334.6°	34.9	372.8°	152.9	406.5°	560.5
274.0	2.0	340.0	41.0	373.2	146.9	407.7	560.8
279.8	4.0	341.4	46.7	373.3	155.4	408.0	560.8
293.7	6.8	341.5	46.4	374.0	158.0	412.5	562.1
294.0	4.3	353.0	55.3	377.3	166.0	413.2	554.6
313.8	5.5	355.5	78.5	379.6	187.0	413.5	556.5
320.8	20.5	356.2	74.8	380.0	192.3	413.5	570.4
325.2	22.5	356.4	78.5	384.1	193.7	414.8	587.3
329.5	29.0	358.5	70.5	389.8	261.5	414.8	588.0
330.2	31.0	361.5	82.5	390.5	270.8
332.7	32.8	372.0	121.5	391.0	262.7

large scale plot like that represented in Fig. 2 was thus obtained. From this plot the pressures were read off at a series of round temperatures



differing by 10° , and the values so read off are given in Table II in the column headed "obs." The column headed "T and H" contains the data obtained by Troost and Hautefeuille.

TABLE II.—VAPOR PRESSURES OF SODIUM HYDRIDE AT ROUND TEMPERATURES.

<i>t.</i>	Obs. $\log_{10} p.$	Calc. $\log_{10} p.$	Obs. <i>p.</i>	T and H.	Calc. <i>p.</i>
290°	0.700	0.718	5.01	...	5.22
300	0.904	0.902	8.02	...	7.98
310	1.094	1.093	12.42	...	12.40
320	1.270	1.275	18.62	...	18.84
330	1.454	1.452	28.45	28.0	28.31
340	1.620	1.6234	41.69	40.0	41.98
350	1.792	1.7894	61.94	57.0	61.58
360	1.950	1.9574	89.13	75.0	90.66
370	2.110	2.1067	128.83	100.0	127.91
380	2.260	2.2586	181.97	150.0	181.39
390	2.410	2.4062	257.0	280.0	254.8
400	2.550	2.5496	354.8	447.0	354.5
410	2.694	2.6888	598.0	488.4
420	...	2.8244	752.0	667.4
430	...	2.9566	910.0	904.9

From these equilibrium pressures and existing data on specific heats, it is possible to evaluate the heat of dissociation and its change with the temperature. The heat of reaction was calculated for the two temperature intervals 340°–350° and 350°–360° by means of the equation

$$2.3 \log_{10} p_1/p_2 = Q_p/R(1/T_2 - 1/T_1);$$

and the average of these values, 14,740 cal., was taken to represent the heat of dissociation of one formula weight NaH at 350°. By combining this with the heat capacity data the change of the heat of the reaction with the temperature was obtained. The heat capacity of liquid sodium has been determined by Bernini,¹ and found to be 7.68 cal. per gram atom. The molal heat capacity of hydrogen was taken to be $6.5 + 0.0009 T$. The atomic heat capacity of hydrogen in its compounds was taken as 2.3, and that of sodium as 6.4, giving 8.7 cal. for the heat capacity of NaH. From these data we obtain the equation $Q_T = 13110 + 2.5T$.

The heat of reaction at ordinary temperature is calculated to be 13,860 cal. per gram atom of sodium. Forcrand² measured the heat of this reaction by dissolving definite portions of NaH in water, and found the heat evolved to be 25,800 cal. per mol. of sodium hydride. The heat of solution of sodium was taken as 42,400 cal. per gram atom of sodium. The heat of formation of sodium hydride is accordingly 16600 cal. This value is considerably larger than that obtained from the equilibrium measurements. Forcrand made four experiments, using 0.0120, 0.0380, 0.0227 and 0.0070 gram of material. According to his value of the heat of reaction the largest quantity used would give to the calorimeter about 40.8 cal., while the smallest quantity would give approximately 7.5 cal.

¹ *Loc. cit.*

² Forcrand, *Compt. rend.*, 140, 990 (1905).

What type of calorimeter Forcrand used is not stated. Neither does he mention the quantity of water used in the calorimeter. The quantity necessary to give one degree rise, assuming the calorimetric apparatus to have zero heat capacity, would be only 40.8 cc. in one case and 7 cc. in another.

By substituting the above expression for Q_T in the thermodynamic equation $d \log p = Q_T/RT^2dT$ and integrating, we obtain the following expression for the dissociation pressure p of sodium hydride at any temperature:

$$\log_{10} p = -5700/T + 2.5 \log_{10} T + 3.956.$$

The values calculated by this equation are given in Table II in the column headed "calc." It will be seen that the deviations between the observed and calculated values seldom exceed 1%.

5. The Equilibrium Pressures of Potassium Hydride.

The observed values of the equilibrium pressures of potassium hydride are given in Table III.

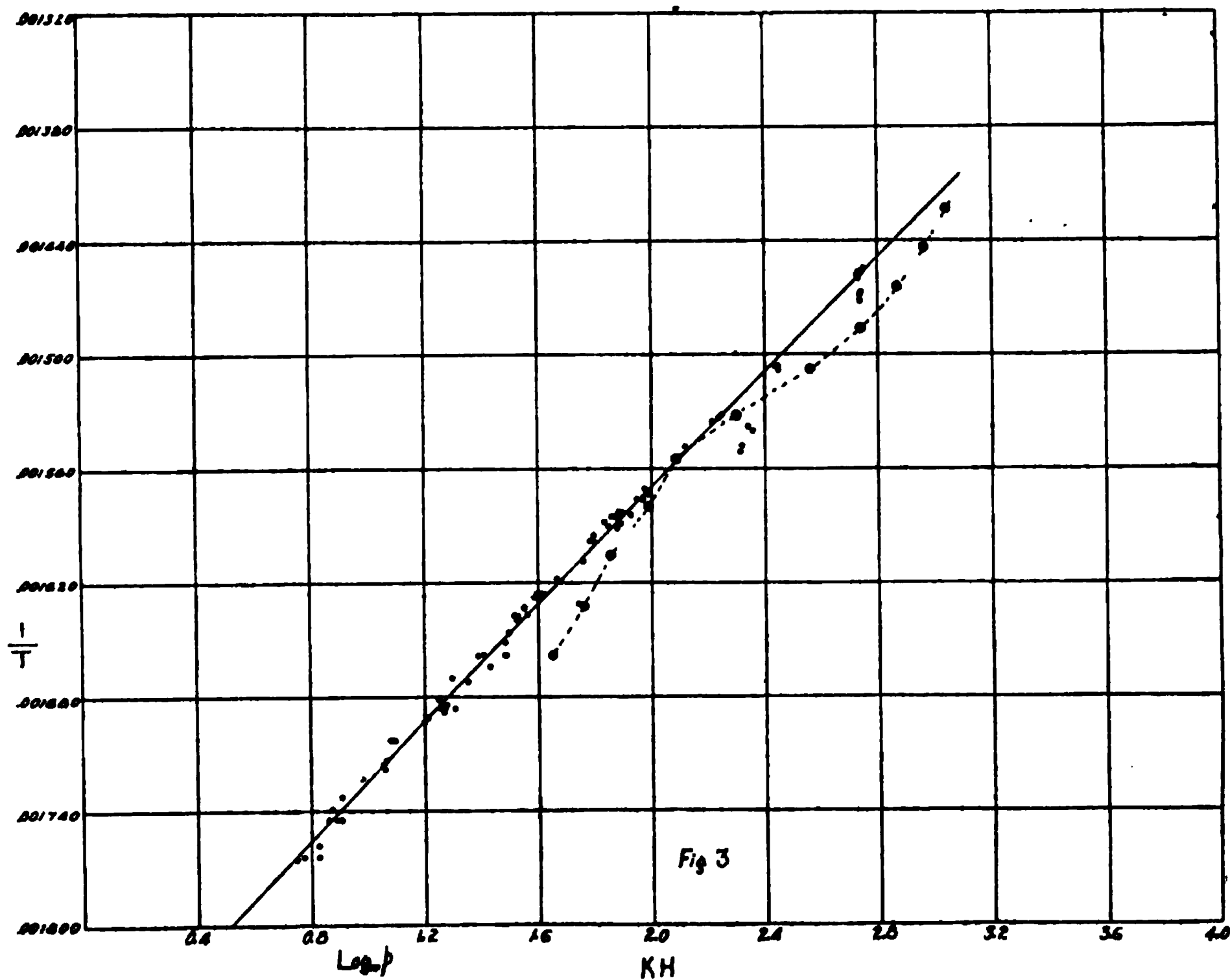
TABLE III.—OBSERVED VALUES OF THE VAPOR PRESSURES OF POTASSIUM HYDRIDE.

t .	p .	t .	p .	t .	p .	t .	p .
215.0°	0.1	319.5°	18.5	341.0°	39.8	377.3°	218.5
250.0	0.5	320.0	18.5	341.5	41.3	376.0	227.5
270.0	2.1	320.8	18.8	342.0	40.2	378.5	164.3
290.0	4.8	321.6	17.9	345.0	46.0	379.0	172.8
293.7	5.6	325.1	22.5	349.0	57.3	380.0	175.8
293.9	6.7	326.2	19.8	353.0	62.3	389.8	279.6
294.0	6.0	328.3	27.0	354.2	62.8	390.5	277.0
295.5	6.7	330.0	27.8	355.5	77.0	391.0	273.0
300.0	7.7	330.2	30.5	356.4	77.5	406.5	541.8
302.0	7.5	330.3	25.7	358.0	73.9	407.7	542.5
304.0	8.1	332.7	30.5	358.5	85.0	408.0	542.7
309.0	11.5	334.6	33.0	359.0	77.8	412.5	539.5
310.0	11.4	337.0	34.0	361.5	91.6	413.2	535.3
311.0	11.6	337.8	33.8	363.0	98.0	413.5	543.0
314.2	12.6	338.0	34.8	364.0	95.0	414.8	563.7
318.1	15.8	339.0	37.3	372.0	205.5
318.5	16.3	340.2	55.5	373.2	208.5

These values were treated according to the same procedure as that followed in the case of sodium hydride. The data were plotted with $\log p$ and $1/T$ as coördinates, as shown in Fig. 3. The equation obtained is:

$$\log_{10} p = -5850/T + 2.6 \log_{10} T + 3.895.$$

The heat of reaction per equivalent of potassium hydride is calculated to be 14,240 cal. at ordinary temperatures. No direct measurement of the heat of this reaction has been previously made. The observed vapor



pressure interpolated for round temperatures and the vapor pressures calculated by the above equation are presented for comparison in Table IV.

TABLE IV.—VAPOR PRESSURES OF POTASSIUM HYDRIDE AT ROUND TEMPERATURES.

t.	Obs. log p.	Calc. log. p.	Obs. p.	T. and H.	Calc. p.
300°	0.866	0.865	7.31	...	7.32
310	1.060	1.053	11.49	...	11.29
320	1.246	1.240	17.62	...	17.38
330	1.426	1.424	26.6	45.0	26.55
340	1.600	1.598	39.8	58.0	39.61
350	1.768	1.770	58.6	72.0	58.89
360	1.934	1.937	85.9	98.0	85.5
370	2.094	2.098	124.2	122.0	125.3
380	2.248	2.255	177.0	200.0	179.89
390	2.404	2.407	253.5	363.0	255.27
400	2.556	2.555	259.74	548.0	258.92
410	2.706	2.697	508.15	736.0	497.73
420	2.852	2.839	916.0	690.24
430	2.998	2.976	1114.0	946.24

6. Summary.

The dissociation pressures of sodium hydride and potassium hydride

between 250° and 400° have been measured; and the following equations expressing them in millimeters of mercury have been derived:

$$\text{For NaH: } \log_{10} p = -5700/T + 2.5 \log_{10} T + 3.956.$$

$$\text{For KH } \log_{10} p = -5850/T + 2.6 \log_{10} T + 3.895.$$

The vapor pressure equations for liquid sodium and potassium have been calculated from the following data: (1) the boiling points of these substances; (2) their heats of vaporization, derived from Trouton's rule (assuming the same constant as for mercury); and (3) the heat capacities of the liquids and the vapor. These equations are

$$\text{For Na: } \log p = -6200/T - 1.35 \log T + 12.4.$$

$$\text{For K: } \log p = -6000/T - 0.40 \log T - 0.0008T + 10.73.$$

The heat of reaction at ordinary temperatures has been calculated from the measurements, and found to be 13,860 calories per formula-weight of sodium hydride (NaH) and 14,240 calories per formula-weight of potassium hydride (KH).

BOSTON, March, 1912.

A CORRELATION OF THE ELASTIC BEHAVIOR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.

BY JOHN JOHNSTON.

Received April 15, 1912.

As is well known, the effect of pressure acting on both the solid and liquid phase of a single substance is to raise or lower its melting point according as the process of melting is accompanied by an increase or a decrease of volume respectively, the latter being the exceptional case. But when pressure acts only on the solid phase, but not—or not to the same extent—on the liquid phase, the melting point is always lowered and by an amount which is many times as great as the corresponding change produced by the same pressure acting on both the liquid and the solid phase. For example, the melting point of ice is lowered by 0.0075° per atmosphere of equal pressure, but by about 12 times as much, or 0.09° per atmosphere, when the pressure acts only on the ice.¹ The latter type of pressure we shall for convenience in what follows designate by the term "unequal pressure."

A study of the work of Spring and others rendered evident a parallelism between the melting point of a substance and the ease with which it will, when subjected to (non-uniform) compression, flow or weld into a more or less solid block; namely, that the higher the melting point of the material, the less readily does it flow, or weld together, under compression.

¹ Cf. J. H. Poynting, *Phil. Mag.*, [5] 12, 32 (1881); Ostwald's "*Lehrbuch der Allgemeinen Chemie*," 2 Aufl., Vol. 2, II, pp. 374-9; or Roozeboom's "*Heterogene Gleichgewichte*," Vol. 1, pp. 213-7.

From this it is obvious that, if it be assumed that the process of flow is a manifestation of a real melting produced by the compression, the pressure must be unequal in character; that is, the pressure acting on the solid must be greater than that on the liquid phase. For, when the same pressure acts on both phases, the melting point of practically all substances is raised, and not lowered, as, on this explanation of the phenomenon, we assume it to be. It seemed of interest, therefore, to calculate the effect of unequal pressure in lowering the melting point of metals, to compute the amount of such pressure required to cause the metal to melt at or about the ordinary temperature, and to investigate if the pressure computed in this way can be correlated with any of the mechanical, or other, properties of the metals.

The equation made use of in calculating the effect of unequal pressure on the melting point is derived most readily in the way employed by G. N. Lewis in a parallel case—the calculation of the variation of osmotic pressure with temperature.¹

Let A be the activity² of the substance in the solid phase, and A' the activity in the liquid phase. Now, if the pressure on the solid phase alone is increased by dP , then the temperature of equilibrium will be changed by an amount dT . Since both phases are initially in equilibrium, the activity of the solid (A) and that of the liquid (A') must be equal; moreover, they must again be equal when equilibrium is re-established. Hence $A = A'$, and $dA = dA'$, or $d\ln A = d\ln A'$.

Now, the change in $\ln A$ is due to temperature change alone; the change in $\ln A'$ is due to change in temperature and change in pressure; that is,

$$d\ln A = \left(\frac{\partial \ln A}{\partial T} \right) dT$$

and

$$d\ln A' = \left(\frac{\partial \ln A'}{\partial T} \right) dT + \left(\frac{\partial \ln A'}{\partial P} \right) dP.$$

Equating the right hand members of these equations, we have

$$\left(\frac{\partial \ln A}{\partial T} \right) dT - \left(\frac{\partial \ln A'}{\partial T} \right) dT = \left(\frac{\partial \ln A'}{\partial P} \right) dP.$$

Substituting for the partial differentials their values from the fundamental thermodynamic equations,³ and combining the left hand terms, gives

¹ THIS JOURNAL, 30, 680 (1908). I am much indebted to Prof. Lewis for bringing to my attention this method, which is so much more succinct than the mode of derivation which I had at first made use of.

² For a definition and discussion of the term "activity," see Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

³ Lewis, equations V and VIII, *Proc. Am. Acad.*, 43, 266, 267 (1907); *Z. physik. Chem.*, 61, 137, 138 (1908).

$$\frac{LdT}{RT^2} = \frac{VdP}{RT}$$

or

$$\frac{dT}{dP} = \frac{VT}{L} \quad (I)$$

where V is the molal volume of the solid phase, T its melting point on the absolute scale (both phases under the same pressure), and L its molal heat of fusion. The quantities V and T are always positive, but L (as here used) is always negative; hence application of excess pressure on the solid phase always lowers the melting point.¹

This differential equation is rigorously correct; but in order to integrate it, we must know how V and L change with the temperature and with the pressure. The variation of V is determined by the coefficients of expansion and of compressibility, which are known for comparatively few substances. With regard to the other factors, our knowledge of L at the ordinary melting point under atmospheric pressure is as yet extremely unsatisfactory in character and limited in scope, while our ignorance of its variation with either temperature or pressure is practically complete. However, in the case of the metals at least, this difficulty is not so serious, as is shown by the following considerations:

The variation of melting point with pressure, acting equally on both phases, for all the metals which have so far been investigated, has been found to be practically linear within the error of experiment.² It is a necessary consequence of this linearity that with increasing pressure the relation between L and $(V-V')$ (V' is the molal volume of the liquid phase) must be linear, or, in the limiting case, remain practically constant. It is, therefore, very plausible that we are justified in assuming that the variation of L with V is linear. Integrating equation I on this basis, between the limits T_1 (the ordinary melting point at 1 atm. pressure,

¹ This lowering is, of course, relative to the melting point when that pressure which now acts on the liquid alone (the solid being subject to pressure in excess of this) acts on both solid and liquid. In other terms: if the melting point is denoted by T with subscripts and superscripts to represent the pressure acting on the solid phase and liquid phase respectively, then $T_{P+\Delta P}^P$ is always lower than T_P^P , the magnitude of this lowering being dependent on the excess of pressure ΔP acting on the solid. Now T_P^P may be higher, or lower, than T_1 (the ordinary melting point at atmospheric pressure), according as the volume change on melting is positive or negative; consequently, in some cases $T_{P+\Delta P}^P$ may be higher than T_1 , but this will be so only when ΔP is small compared to P , a contingency which, we believe, does not affect the main considerations advanced in this paper.

² Tammann, *Z. anorg. Chem.*, 40, 54 (1904) with K and Na; Johnston and Adams, *Am. J. Sci.*, 31, 501 (1911); *Z. anorg. Chem.*, 72, 11 (1911), with Sn, Bi, Cd, Pb at pressures up to 2000 atm.; Bridgman, *Proc. Am. Acad.*, 47, 347 (1911), with Hg up to still higher pressures.

expressed on the absolute scale) and a given temperature θ , we obtain the equation

$$P = \frac{L}{V} \ln \frac{T_1}{\theta}. \quad (\text{II})$$

Instead of the molal values we may substitute the heat of fusion (Q_1) per gram of substance, and the density (D_1) of the solid, at the ordinary melting point¹ (T_1); making the necessary transformations, we obtain finally the equation

$$\varphi = 95.1 Q_1 D_1 \log \frac{T_1}{\theta}, \quad (\text{III})$$

which enables to calculate the melting pressure (φ , expressed in atmospheres) corresponding to the temperature θ ; that is, φ is the pressure required to cause the substance to melt at the absolute temperature θ .

This formula has been applied to the calculation of the excess pressure (acting on the solid only) required to cause the metal to melt at 27° (that is, $\theta = 300^\circ$) in the case of all the metals² for which values of Q are given in Landolt-Börnstein-Meyerhoffer Tabellen (2 Aufl., p. 470). For some metals more than one value is given, but it is at present impracticable to determine which are most reliable; for this reason, the mean value was adopted in all such cases. For the same reason, the general mean value of the density, as given in the tables (pp. 224-9), was taken. The melting points are those now generally adopted.

The data and results are brought together in Table I, in which the metals are arranged in the order of increasing values of the melting pressure calculated in this way from equation III. It was conjectured that this order might bear some relation to that obtained when these metals are arranged with reference to the relative values of their elastic constants and mechanical properties.

¹ In the computations which follow, the value of the density at the ordinary temperature was used. This was done because of the uncertainty in the appropriate correction; moreover, our present knowledge of D at the ordinary temperature is so unsatisfactory that it would be altogether futile to apply any such correction, especially as the accuracy of the present values of Q is so doubtful.

² Excepting iron, on account of the uncertainty of what "iron" is, and the disparity of the recorded values. The value given for nickel in Landolt-Börnstein-Meyerhoffer Tabellen (p. 470) as a heat of fusion (taken from Pionchon, *Ann. chim. phys.*, [6] 11, 106 (1887)) was found, on reference to the original, to be a heat of *transformation* (occurring somewhere between 230° and 400°); consequently nickel could not be included. (Similarly, Pionchon's values for iron given in *L.-B.-M.* (p. 470) are heats of *transformation*.) Mercury and gallium are omitted, since they are liquid at ordinary temperatures. The value of Q for aluminium is somewhat doubtful; it was calculated from the "total heat" (as given in *L.-B.-M.*) by means of the specific heat of aluminium (0.30) as given by Bontschew (*L.-B.-M.*, p. 383). No alloys could be included owing to lack of the necessary data; in any case the formula is applicable only to those alloys which melt completely at a definite temperature.

TABLE I.—LOWERING OF MELTING POINT OF METALS EFFECTED BY ONE ATM. UNEQUAL PRESSURE, TOGETHER WITH THE COMPUTED MELTING PRESSURES AT ORDINARY TEMPERATURES.

Metal.	Melting point.		Heat of fusion. Q	Density. D	ΔT_1^1	ϕ_{π}^2
	t	T_1				
K	62	335	15.7	0.87	0.59	64
Na	97	370	31.7	0.98	0.29	266
Pb	327	600	5.4	11.37	0.24	1760
Sn	232	505	14.1	7.29	0.12	2200
Bi	270	543	12.5	9.80	0.11	3000
Cd	321	594	13.7	8.64	0.12	3300
Al	658	931	42.0	2.60	0.21	5100
Zn	419	692	28.0	7.1	0.084	6900
Ag	960	1233	23.0	10.50	0.12	14000
Cu	1083	1356	43.0	8.93	0.086	24000
Pd	1550	1823	36.3	11.4	0.11	31000
Pt	1755	2028	27.2	21.5	0.084	46000

The most obvious mechanical property with which to compare the series of ϕ values is the flow pressure.³ This was determined for a series of metals, by Tammann, Verigin and Levkojeff;⁴ later, and independently, by Kurnakov and Zhemchuzhny.⁵ Arranged in the order of decreasing ease of flow, the metals follow in the order K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb, a sequence which is identical with that deduced thermodynamically and presented in Table I. But not only is the sequence of ϕ values identical with that of the flow pressure; it is practically identical with the sequence obtained when the metals are arranged in the order of any of their elastic properties for which measurements have been made. This is shown by Table II, in which have been brought together all the

¹ This column, which represents the melting point depression produced by 1 μ m. excess pressure acting on the solid, is added merely to give an idea of the magnitude of this quantity. The values given are calculated from the formula $\Delta T_1 = T_1 / 41^9 QD$ which is easily derived from equation I.

² It should be observed that the values of ϕ given in the preliminary note (*Washington Acad. Sci.*, 1, 260 (1911)) were calculated by a formula which holds strictly only so long as ϕ , or the difference between T and θ , is small. The more accurate mode of calculation from equation III of the present paper leads to somewhat higher numerical values of ϕ , but does not alter the order of the ϕ values; so that this change does not affect the argument.

³ The amount of compression required to cause a material to flow is characteristic of the material under specified conditions; but at constant temperature it varies, as is obvious, with the size of the aperture through which the flow takes place; probably also it depends upon the shape of the aperture and upon other subsidiary factors. Hence, determinations of flow pressures are comparable only when they have all been made in the same apparatus and in the same way. This condition is fulfilled by the experimental observations cited, which lead to reliable relative values of the flow pressure for a series of metals.

⁴ *Ann. Physik*, 10, 649 (1903).

⁵ *Z. anorg. Chem.*, 64, 174 (1909).

data available on the elastic properties, namely, compressibility, hardness, tensile strength, elastic limit, elastic modulus and modulus of rigidity.

TABLE II.—RELATIVE VALUES¹ OF THE ELASTIC CONSTANTS OF METALS.

Metals in order as in Table I.	Compressibility. (a).	Hardness. (b).	Tensile strength.		Elastic limit.			Elastic (Young's) modulus. (g).	Rigidity modulus.	
			(c).	(d).	(e).	Lower. (f).	Upper. (f).		(h).	(i).
K	31.5	0.5
Na	15.4	0.4
Pb	2.2	1.5	2.0	21	0.3	25	102	17	5	0.80
Sn	1.7	1.8	2.1	36	4	34	55	34	16	1.50
Bi	2.8	2.5	32	12	..
Cd	1.9	2.0	..	48	..	28	109	71	17	2.31
Al	1.3	2.9	283	600	70	29	2.55
Zn	1.5	2.5	13	..	10	125	770	78	31	..
Ag	0.84	2.7	22	272	12	70	39	2.67
Cu	0.54	3.0	25	316	12	203	2780	108	42	4.37
Pd	0.38	4.8	27	103	46	..
Pt	0.21	4.3	29	..	26	161	52	6.46

From this table it is evident that, as the value of ϕ increases, the compressibility decreases, and the values of the other elastic properties increase steadily. The exceptions to this statement are very few as regards any one property, and vary irregularly as we pass from one property to another; in other words, there are no systematic divergences between the sequence of the metals as derived from the thermodynamic relationship discussed in this paper, and that obtained when they are arranged progressively with reference to any one of their elastic properties. The slight divergences are no greater than one might expect from the uncertain character of the thermal data, on the one hand, and of the elastic constants on the other. Indeed, excellent agreement could have been obtained by selecting for each metal an appropriate value from the somewhat discordant data for the elastic constants in the Landolt-Börnstein-Meyerhoffer Tabellen; but it was deemed more commendable to take a general mean of all the values there given, as it was impracticable to determine just

¹ It is to be noted that the values given in the table are *relative* only, and are not always expressed in the same units (e. g., columns c and d, e and f, h and i).

(a) As given by Richards and collaborators, THIS JOURNAL, 31, 156 (1909).

(b) According to Rydberg, *L.-B.-M. Tabellen*, p. 57.

(c) *L.-B.-M. Tabellen*, p. 53.

(d) Wertheim (1848) quoted by Faust and Tammann, *Z. physik. Chem.*, 75, 118 (1911).

(e) *L.-B.-M. Tabellen*, p. 53.

(f) As determined by Faust and Tammann, *loc. cit.*

(g and h) General mean of the (sometimes very discordant) values given in *L.-B.-M. Tabellen*, pp. 43-45.

(i) Horton, *Trans. Roy. Soc. London*, (A) 204 (1905).

which values represent most accurately the true elastic constants of the various metals.

The purely elastic properties of metals have often been collated and compared, and it has been surmized repeatedly that these properties are some function of the melting point of the metal.¹ But, so far as the writer is aware, no one has advanced further than a statement of the general parallelism between elastic properties and melting point—a statement to which there are some notable exceptions (lead, aluminum (see Table II), also a large number of alloys), which seriously limited its scope and usefulness. When arranged with reference to the function of the melting point deduced in this paper, the above two metals cease to be exceptions.²

One other piece of presumptive evidence in favor of this point of view may also be mentioned, namely, a comparison of the values of ϕ with the flow pressures of tin as determined by E. Jänecke³ at a series of temperatures. In default of knowledge of the variation of Q with temperatures and pressure, we may justifiably consider Q and D as constants. For any one metal therefore, equation III may be written, since T_1 is also constant,

$$\phi = K_1 - K_2 \log \theta \quad (\text{IV})$$

where K_1 and K_2 are constants, the values of which depend upon Q , D , and T_1 . The graph of equation IV, which gives the variation of ϕ with θ , is very similar to the curve plotted from Jänecke's results; with increasing temperature both diminish at about the same decreasing rate.

From the above, then, it appears to be true that the mechanical properties of metals are correlated with the amount of pressure—assumed to act on the solid alone—requisite to cause the metal to melt at or near the ordinary temperature. This pressure in turn depends upon the melting point, the density, and the heat of melting of the metal. The first two of these quantities are known to be periodic functions of the atomic weight, and there is every reason to believe that the heat of melting, and therefore also ϕ , is. Therefore, reasoning from the observed parallelism, we should expect some, or all, of the elastic properties to be periodic functions. So far, thorough measurements have been made only on the compressibility, which, according to Richards, shows marked periodicity.

The remarkable concordance shown in the above table, which can

¹ No references are given to this, because the author found it impracticable to examine all of the voluminous literature in order to determine with whom each particular suggestion originated. Some of the points are discussed by Kurnakov and Zhemchuzhny (*Z. anorg. Chem.*, 60, 1 (1908); 64, 149 (1909)).

² The formula III could not be applied to alloys owing to lack of the necessary data. In any case the formula is applicable presumably only to such alloys as melt completely at a constant and definite temperature.

³ *Metallurgie*, 8, 68–72 (1911).

hardly be due to coincidence, suggests that the "flow" of metals—or indeed, every *permanent* distortion of a crystallin solid—is due to an actual fusion (with subsequent resolidification) of the crystals. The validity of this view is supported by a large number of well known facts, *e. g.*, that a metal requires progressively less effort to cause it to weld—or to forge it—the higher its temperature. Moreover it is corroborated by a large number of observations, which demonstrate the existence of important differences between metal which has "flowed" or has been subjected to deformation of any kind and the same metal in the annealed condition.

All the available evidence¹ goes to show that there is: (a) a difference in the energy content of the strained and unstrained metal, which is manifested in a difference between the two forms, (1) in their electrolytic potential when immersed in a solution, (2) in their thermoelectric power, (3) in their heat of solution; (b) a difference in structure manifested in differences in (1) microscopic appearance, (2) mechanical properties—hardness, tensile strength, etc., (3) density,² (4) conductivity for heat or electricity, etc. For any one metal these differences vanish about a single temperature common to all,—thus for silver at about 260°—that is, at the temperature at which annealing proceeds with appreciable rapidity.

According to Beilby,³ the process of deformation is always accompanied by a partial transformation of the metal to an "amorphous"⁴ form, which acts as a cementing material for the untransformed grains. According to Faust and Tammann,⁵ on the other hand, the change of properties on deformation is parallel to the production of smaller crystallites. Whichever be the correct interpretation—if indeed these views are mutually exclusive⁶—the fact remains that deformation of a metal is accompanied by changes in its properties. These changes are such that they would be rather difficult to account for reasonably, except on the very simple supposition that an actual melting has occurred.

Against this view it might be urged that the pressures required to cause the metals to melt about the ordinary temperature are so great that they are unlikely to occur in practice. But this objection loses

¹ Cf. G. T. Beilby, *Phil. Mag.*, [6] 8, 258-76 (1904), who discusses the evidence in detail.

² Kahlbaum, Roth and Siedler, *Z. anorg. Chem.*, 29, 197 (1902); Kahlbaum and Sturm, *Ibid.*, 46, 217 (1905); Spring, *J. chim. phys.*, 1, 593 (1903); *Rec. trav. chim.*, 23, 1 (1904). This subject is fully discussed by Johnston and Adams, *THIS JOURNAL*, 34, 563 (1912).

³ *Loc. cit.*

⁴ Beilby here uses the term "amorphous" to denote "a heterogeneous assemblage of molecules."

⁵ *Z. physik. Chem.*, 75, 108-26 (1911).

⁶ Cf. *postea*, p. 800.

weight when it is remembered that the brunt of any strain, to which a crystallin mass is subjected, is borne by a small number of crystals at any one time. When these crystals give way, others take up the strain, and so on. In this way, relatively very small total forces could produce very considerable pressures locally, pressures sufficient to cause melting at those points. This process would be like the method of tearing a pack of cards, which consists in holding them in such a way that the force comes on only one card at a time.

This point of view accounts plausibly for other aspects of the behavior of metals—for instance, the “hardening” of metals and the increase of strength following upon deformation; but before proceeding to discuss this, it seems advisable to outline a mechanical picture of the probable mode of action of unequal pressure upon a metal.

Poynting¹ and also Le Chatelier² have used this conception of unequal pressure to account for regelation—the consolidation of a mass of loose snow at 0° into a block of solid ice. The pressure, due to the superincumbent material, lowers the melting point at the surface of contact of adjacent grains by an amount Δt . The water formed flows out into the interstices of the snow grains, where it is at a pressure of 1 atm. but at a temperature of $-\Delta t$, and is in contact with ice at 0°; consequently it freezes again. This process continues until all the interstices are filled up; that is, until a solid block of ice is formed.

Considerations analogous in every respect are applicable to systems of solid grains in contact with water or an aqueous solution. In such cases pressure acting only on the solid increases its solubility, and renders the solutions supersaturated as soon as they are out of contact with the *compressed* solid. Le Chatelier accounts in this way for the consolidation of natural beds of rock-salt, gypsum, calcium carbonate, etc.; and he showed by direct experiment that consolidation could be produced in this way.

The behavior of metals under the action of a differential compression we conceive to be identical with that pictured above for ice. Namely, that metal melts wherever the pressure reaches the appropriate value, flows into the interstices where the pressure is smaller and solidifies again, with the formation in general of very small crystals, by reason of the exceedingly rapid rate of recrystallization.

The effects of unequal pressure are analogous to those produced by a shearing stress; or perhaps one should say rather that the effects of a shearing stress are those produced by what we have termed unequal pressure. Now a longitudinal tensile stress can always be resolved into a uniform dilatation and a shearing stress, just as a longitudinal compres-

¹ *Phil. Mag.*, [5] 12, 32 (1881).

² *Z. physik. Chem.*, 9, 338 (1892).

sive stress can be regarded as composed of a uniform compression and a shearing stress. Hence the conception of unequal pressure, and its effect on the melting point of a crystallin substance, is equally applicable to all permanent deformations, whether produced by compression or by tension.

When pictured in the way outlined in the above paragraphs, it is obvious that one might expect a parallelism between the ϕ values and certain of the mechanical properties: in all cases, namely, in which the property in question—for instance, tensile strength or flow pressure—implies in any way a permanent deformation of the material, the latter being presumed always to be a manifestation or a real melting produced wherever the stress reaches the appropriate value. In regard to the purely elastic properties—those, *e. g.*, compressibility, which imply no *permanent* change in the material—the parallelism can hardly be ascribed to a melting; but it may very well be an expression of the fact that the elastic properties and the ϕ values as calculated in this paper are all functions of some one determining factor.¹ But even if this is so, it in no wise detracts from the plausibility of the view that deformation is conditioned by an actual melting; for there is no apparent necessary connection between the modes of action of stresses which produce deformation and of those which do not.

The possibility of accounting in this way for the flow of solids was considered by Tammann,² but summarily rejected by him on what appear to the writer to be insufficient grounds. In the first place he doubts the thermodynamic admissibility of the derivation of the formula for the lowering of equilibrium temperature by unequal pressure. In the second place, in his experimental work he was unable to detect any discontinuity in the rate of flow at the pressure indicated by the formula as the melting pressure at that particular temperature. To reason from this lack of discontinuity that the effect of unequal pressure upon the melting point is illusory might be justifiable if Tammann had been dealing with a single crystal; but dealing as he was with a conglomerate of crystals, flow began whenever the pressure on any one of them exceeded the melting pressure under the particular conditions. Indeed the behavior of ice in this respect is precisely similar to that of the metals—a fact specifically noted by Tammann himself—the only difference being that the absolute values of the pressure are lower than for the common metals.

Tammann concludes:³ "From the work on the velocity of flow of crystallin substances it follows that the flow is not conditioned by a previous

¹ This question is treated later, p. 801.

² *Ann. Physik*, [4] 7, 198 (1902); *Krystallisieren und Schmelzen* (Leipzig, 1903), pp. 173–81.

³ *Loc. cit.*

melting, but that the *plasticity, the reciprocal of the viscosity, is a property characteristic of the substance.*" In order to account for the fact that the velocity of flow, and hence the "plasticity," of ice increases very considerably with the pressure, it must be assumed that its viscosity diminishes greatly with pressure. This assumption may hold, for water at low temperatures and low pressures is an exception to the general rule that the viscosity of liquids is increased by pressure;¹ to the writer nevertheless it seems less forced to account for the flow by the aid of the argument advanced in this paper: namely, that flow is the result of a partial melting. On this basis we can readily see why increased pressure, which causes more ice to melt and hence increases the amount of water present, should increase the plasticity. Moreover, so far as the writer has been able to ascertain, this explanation conflicts with none of the recorded observations on the flow either of ice or of any other substance. Indeed it receives direct confirmation from some recently published work of Hess on the plasticity of ice;² he found, as Tammann previously had also observed, that at a given temperature a considerable movement of the plunger takes place under a pressure much lower than that deduced thermodynamically (on the assumption that the pressure acts *equally* on both the ice and the water produced by the melting), and presents indisputable evidence that the ice in these circumstances had actually melted.

The mode of action outlined in this paper, besides accounting plausibly for the magnitude of some of the mechanical properties of metals, can also be adduced to explain observations on the structure of metal which has "flowed," or has been subjected to deformation of any kind. The process of "flow," or of deformation, of a metal is always accompanied, as we have seen, by a number of changes, among others by a "hardening" of the metal; this term is used to denote an increased resistance to stress, and is in one sense unfortunately chosen, for Faust and Tammann³ have shown that in some cases the "hardness," as measured by the sclerometer, is not affected by the process of "hardening." Faust and Tammann, by microscopic observation of the specimens, were able to determine with a precision of about 1% the pressure or tension required to produce the first permanent deformation of a number of metals; and found that this lower elastic limit is the same for pressure as for tension. Further slow increase of pressure above the lower elastic limit causes this limit to recede to higher pressures; until finally an upper elastic limit, the flow pressure, is reached. This again shows that increase of pressure produces an increased rigidity of the metal; which is in accordance with the idea, first enunciated by Beilby, that the change in properties of

¹ R. Cohen, *Ann. Physik*, 45, 666 (1892); Hauser, *Ibid.*, 5, 597 (1901).

² *Ibid.*, 36, 449-93 (1911).

³ *Z. physik. Chem.*, 75, 118 (1911).

metals on hammering, rolling, etc., is a direct consequence of the deformation which occurs during the process.

Now these facts accord well with the argument of the present paper; for, exactly as in the case of the consolidation of loose snow to a block of ice, as soon as the stress reaches an appropriate value (the lower elastic limit), melting and flow into the interstitial spaces take place, with immediately subsequent recrystallization; this process continues until this flow is no longer possible (the upper elastic limit), whereupon increased stress produces rupture of the material. Now, the actual process of flow diminishes the volume of the spaces into which flow is possible, and to this extent diminishes the inequality of pressure acting on liquid and solid; hence it requires progressively higher pressures absolutely (though at the same temperature the same *excess* of pressure on the solid) to produce flow; in other words, the rigidity of the material is increased.

A phenomenon analogous in every respect to that observed by Faust and Tammann has been recorded by Bridgman¹ in some very recent work on the collapse of thick walled cylinders under high hydrostatic pressure. Bridgman found, namely, that with every successive application of pressure, yield is not resumed until the previous pressure maximum has been reached or exceeded; this behavior is just what we should expect if flow is conditioned by a true melting.

It is important to observe, in passing, that uniform (hydrostatic) pressure is without *permanent* effect on the properties of metals. Thus Faust and Tammann found that the elastic limit of metal which had been subjected to high hydrostatic pressure remains unchanged; while, as regards the physical properties (density, etc.) it is generally recognized that the only effect of hydrostatic pressure is a temporary change in these properties, which vanishes again whenever the pressure is removed. In all discussions of the effect of pressure, therefore, it is essential that we distinguish carefully between uniform and non-uniform compression, since their effects are so dissimilar.

It is a well known fact that the resistance to flow of eutectics (which are always fine grained) is always greater than that of their components;²

¹ *Physic. Rev.*, 34, 1 (1912).

² This was demonstrated conclusively by Kurnakov and Zhemzhuzhny (*Z. anorg. Chem.*, 60, 1 (1908); 64, 149 (1909)), who present results—in part from the literature, in part original—for a large number of alloys (and also for some pairs of organic substances) which demonstrate this fact. It has been further confirmed by Tammann, who recently (*Nachr. Ges. Wiss. Göttingen*, 1911, 181) described experiments with a few alloys, carried out in quite a different way, from which he draws the conclusions that this increased strength is a direct consequence of the fact that the alloys are finer grained than their components (but offers no explanation as to why a fine grained conglomerate should be stronger than one composed of coarser particles); further that the increased strength of metals which have been chilled is a direct consequence of the decreased size of the grains produced by rapid cooling of the melt.

further, that the varieties of steel possessing the greatest tensile strength (*e. g.*, vanadium steels) are very fine grained. From the standpoint adopted in this paper one might reason that such metals are strong *because* they are fine grained; hence, if we wish to make a steel of high tensile strength, we should endeavor to obtain a very fine grained structure, producing this by whatever means (addition of foreign material, heat treatment or mechanical treatment) may be found suitable for this purpose.

It was noted above that the deformation of metals is accompanied by the appearance of an "amorphous" phase, according to Beilby; by the production of smaller crystallites, according to Faust and Tammann. Neither author speaks definitely of the mode in which the change takes place, nor do they, as far as one can judge, consider it as a manifestation of real melting, with immediately subsequent resolidification. When looked at in this way the divergence between their points of view disappears. For, as is well known, the size attained by a crystal depends, *ceteris paribus*, on its rate of formation; so that Beilby, with presumably a relatively rapid rate of recrystallization, obtained in his flowed metal crystals so small that the metal was apparently "amorphous"; Faust and Tammann, on the other hand, using a totally different method in which the rate of recrystallization was presumably not so great, obtained relatively larger crystal particles.

A point worth mentioning in this connection is this, that the appearance of the cut and polished surface of a metal is not necessarily an altogether fair criterion of the structure of the massive metal. For, as Beilby has demonstrated conclusively, the process of polishing (and obviously, of cutting also) is the result of flow; while in accordance with the viewpoint presented in this paper, flow is the result of a partial melting. Therefore, it is a safe assertion that between the apparent structure of the polished surface and the actual structure of the massive metal, there must always be some differences, which may be so large that examination of the surface only would lead to totally misleading conclusions with regard to the structure of the massive metal.

Kurnakov and Zhemzhuzhny¹ made parallel measurements of the electrical conductivity and flow pressure of series of binary alloys, and found that for given binary systems minimum conductivity and maximum flow pressure occur at the same composition. This exemplifies the general rule that the conductivity of an alloy is less than that of its component metals. Moreover the conductivity of a metal generally decreases when the metal undergoes deformation (*e. g.*, drawing to wire, hammering, or rolling). Now if we interpret these facts with the aid of the idea that the specific conductivity of a given material diminishes

¹ *Loc. cit.*

progressively, other things being equal, with the size of the component particles—an idea which is substantially correct for powdered metals—we find them to be in complete harmony with the conclusion reached on other grounds: namely, that the size of grain of alloys or of metal which has been deformed is less than that of the pure annealed metals.

Summary and Conclusion.

In the foregoing pages we have discussed the idea that the “flow,” or permanent distortion, of metals is conditioned by a real melting, not of the whole mass of metal at any one instant, but of successive groups of particles (namely, those on which the brunt of the strain momentarily falls); and have shown how this idea serves to correlate some properties of metals which at first sight would appear to bear no relation to each other. It leads, namely, to the fact that there is a parallelism between all the elastic properties of metals for which quantitative measurements have been made and the pressure—assumed to act on the solid phase, but not, or not to the same extent, on the liquid phase—which is required to lower the melting point to ordinary temperature. This pressure is a function of the melting point, latent heat of melting, and density at the melting point, of the metal; hence, if these quantities are known for any substance, we can predict the relative order of magnitude of any of its properties which imply deformation of the material.

The same mode of reasoning is equally valid for any crystallin substance, and could be applied to all salts (including silicates and other geologically important substances) if the necessary data were available. At the present time, values of the latent heat of melting are few and far between, so that no general discussion of this part of the subject is practicable now.

The equation discussed in this paper cannot be applied to glasses; for since they are merely supercooled liquids, the value of Q is zero and hence dT/dP is infinit. But this is not so contradictory as at first sight it may seem; for glasses behave as liquids of exceedingly high viscosity, provided always that, conformably with this high degree of viscosity, sufficient time be allowed for the motion to take place.

In conclusion, let us give a brief indication of a connection between the relations discussed in this paper and the conception of “molecular vibration frequency,” a conception which has been very fruitful in the hands of Nernst,¹ Lindemann,¹ Grüneisen,² and others. It has been established, namely, that a large number of apparently diverse physical properties of a substance—melting point, specific heats, coefficients of thermal expansion and compressibility, electrical resistance—may be

¹ This work has been published in a series of recent papers which have appeared in *Sitz. Akad. Wiss. Berlin, Ann. Physik, Z. Elektrochem., and Physik. Z.*

² *Ber. physik. Ges.*, 1911, 426, 591.

considered to be functions of a characteristic quantity, the molecular "vibration frequency."¹

Expressions containing this quantity have been derived by means of which the actually observed variation with temperature of certain of the above properties can be reproduced with remarkable accuracy. Now the flow pressure ϕ at the temperature t is determined by a complicated expression, the value of which depends upon t , T_1 (the ordinary melting point), L (the heat of melting at T_1), V (the specific volume at T_1) and upon the variation of L and V with pressure and temperature; that is, for any particular substance, ϕ depends upon the above constant quantities and upon the specific heats and coefficients of thermal expansion and of compressibility; each of these quantities is some function of the "vibration frequency," consequently the flow pressure ϕ is also a function of this same characteristic parameter.

In view of the state of our knowledge (at the best, very approximate only at the present time) of the experimental data and of certain of the relations involved, it seems premature to endeavor to deduce a definite mathematical relation between ϕ and the frequency, or even to determine the exact form of the function. The existence of such a relationship accounts simply for the parallelism between the calculated ϕ values (of Table I) and the mechanical properties of metals brought together in Table II; for all of these quantities are functions of the vibration frequency, a fact which indicates that all the mechanical properties of metals will be found to be periodic functions of their atomic weights, since the vibration frequency itself is doubtless such a periodic function.

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SULFIDE OF TELLURIUM.

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When hydrogen sulfide gas is passed into a slightly acid solution of tellurous acid or the solution of a tellurous salt, a dark colored precipitate is formed and continues to separate as long as any tellurium remains in the solution. At the moment of formation this precipitate is dark reddish brown in color, but after a short time it becomes still darker, until it is quite black. When dried and heated the substance softens, and on cooling forms a gray, somewhat lustrous mass. On being heated still higher it gives off sulfur.

¹ For a discussion of the exact significance of this quantity, the reader may be referred, in addition to the papers cited above, to recent papers by Einstein in *Ann. Physik*.

These facts were known to Berzelius¹ as early as 1826, and as he found by analysis that the precipitate formed in the manner described contained sulfur and tellurium in the ratio required for the compound TeS_2 , he announced the discovery of that compound, and described its physical properties and the method of its formation, and considered the reaction between hydrogen sulfide and tellurous acid to have the form expressed by the equation



For fifty years after the publication of Berzelius' work no further attention seems to have been given to the reaction between tellurium and sulfur, and it was not until 1876 that the results of any further studies were published. In that year Becker² announced some experiments which showed that the precipitate supposed by Berzelius to be TeS_2 was in reality only a mixture of tellurium and sulfur in those proportions, carbon disulfide dissolving out the sulfur from the material, and thus proving that no chemical union existed. Becker also analyzed the precipitate formed, and confirmed Berzelius' results in regard to its constituents being present in the ratio required for the formula TeS_2 , but instead of the reaction taking place as supposed by Berzelius, Becker assumed that the reduction of the tellurous acid took place in the manner expressed in the reaction



which will be seen to equally well explain the ratio of sulfur to tellurium found to exist in the precipitate.

Becker stated his conclusions as follows: "In any case we can draw the conclusion from these observations that the precipitate with hydrogen sulfide cannot be a compound, but must be a mixture of tellurium and sulfur in constant relations." He also states, however, that he thinks it likely that at the moment of decomposition of the tellurous acid by hydrogen sulfide a sulfurous compound of the tellurium forms, only to decompose quickly.

Since the publication of Becker's results, several workers have contributed to the subject, notably Brauner³ and Gutbier.⁴ No proof has been given, however, to show that a compound of tellurium with sulfur can exist, and the results of these later studies confirm Becker's conclusion in regard to the dissolving out of the sulfur, and of the mass being but a mixture of free sulfur and tellurium in constant proportions.

The first experiments of the writer, in the attempt to find whether or not a true compound of sulfur with tellurium could exist, were made by

¹ *Ann. chim. phys.*, 8, 411.

² *Ann.*, 180, 257.

³ *J. Chem. Soc.*, 67, 545.

⁴ "Studien über das Tellur," p. 51.

varying very widely the conditions under which the precipitation of the tellurous solution took place, in the hope of thus finding some set of conditions which would be favorable to the permanency of the TeS_2 , if such compound was truly at first formed. These experiments, wholly without result as far as finding such conditions was concerned, will be briefly described, as they throw light on the more successful quantitative experiments which were later taken up.

The conditions which were varied in the course of these first experiments were (a) light, (b) heat, (c) pressure, (d) presence of acids in the solution precipitated, (e) presence of salts in the solution precipitated, (f) presence of water. The manner of carrying out some of these experiments, and the results achieved, were as follows:

The darkening of the precipitate formed by hydrogen sulfide a few moments after its formation suggested a possible analogy to the darkening of silver chloride, and it accordingly seemed desirable to see if in the case of the tellurium compound light had anything to do with the change. Three experiments were tried, in each case the solutions being prepared, the precipitation being effected, and the drying of the solid taking place, in the complete absence of light. The dry precipitates were found to be black, and the sulfur was found to be readily extracted by carbon disulfide, showing that even in the absence of light no permanent compound of tellurium with sulfur was formed.

A considerable number of experiments differing widely in their details were tried in the attempt to prepare a stable combination of sulfur with tellurium by keeping the temperature as low as possible. In one experiment, the hydrogen sulfide gas, after being cooled to -10° by being passed through tubes immersed in a freezing mixture of ice and salt, was caused to bubble through a solution of tellurous acid maintained at 0° by being surrounded by a bath of water containing ice. When the precipitation was complete the liquid was filtered (the filter and funnel having been previously chilled by passing iced water through them) and the precipitate was at once transferred to a desiccator which had stood for several hours previously in a box packed with ice. The desiccator and its contents were then maintained at 0° for eighteen hours, until the precipitate seemed to be dry. It was found to consist of sulfur and tellurium, uncombined. In another experiment, tellurous acid was added to alcohol and cooled to -10° , and hydrogen sulfide at -20° was passed into the alcohol mixture. A precipitate resulted as in the previous cases but, after careful drying, it too was found to consist of sulfur and tellurium, in the state of simple mixture. In yet another experiment, advantage was taken of the direct vaporization of ice to free the solid of its admixed water, the filtered precipitate from a solution of tellurous acid being at once frozen, and exposed for several hours

to a current of air brought to the temperature of -10° by passing through an ice-salt freezing mixture.

In none of these cases was it possible to obtain a substance which would not allow sulfur to be readily removed from it by carbon disulfide. One fact, however, was noted which proved to be of great assistance in later work, and this was, that the changing color of the precipitate from brown to black took place much more readily at high temperatures than at low. When the solutions were kept at 0° , several hours might elapse before the precipitate became black, while at higher temperatures several minutes sufficed to bring about the change. The final solution of the problem in regard to the existence of a chemical compound of sulfur and tellurium was directly connected with this observation, as will be brought out when further experiments, carried out quantitatively, are described in a later part of this paper.

Experiments made under decreased pressure, and other tests made in absence of acids or dissolved salts, and where only traces of water vapor were present, were alike without results in obtaining a compound of tellurium and sulfur. Many other experiments were tried along the same general lines as those which have been already noted, and the physical conditions surrounding the solution of tellurous acid at the time of precipitation, and the conditions under which the precipitate was filtered off and dried, were varied through the widest limits, and particular care was given to every detail that might bring about increasing stability in the substance formed. Since all these experiments gave negative results, not offering in any case even the slightest evidence of a combination between the sulfur and tellurium, the conclusion reached by earlier workers seemed inevitable, and the hope of proving that a combination between the two elements could truly exist seemed unwarranted. One line of study, however, still presented itself, and further experiments seeking to explain the phenomena which had been noted in regard to the slow change of color of the precipitate in solutions which had been kept at 0° were taken up. Tests were first made to determine the relative lengths of time which elapsed before the precipitates would turn black, in solutions at known temperatures. This matter was tested for every five degrees between 0° and 100° , and it was found that the change in color from brown to black which took place almost instantly at 100° , required increasingly longer time as the temperature became lower, until about four hours was required when the solution was kept at 0° . The change in color from brown to black being a progressive one, consisting of a slow darkening without any accompanying phenomena which could be used as points of reference, it was naturally very difficult to say when it was complete, and the results of these experiments were therefore not very concordant except as showing the marked difference be-

tween the rapidity of the change at high temperature and the slowness with which it took place at temperatures near 0° .

In the light of these experiments, the previous results obtained in most of the other determinations performed in the course of this work, and of the published writings of others on this subject, became clear, since it is evident that the drying of the precipitate in a steam oven at 100° would bring about its decomposition even if it existed as a compound when the drying commenced, while in the case of those other experiments where the material was dried at a low temperature in a desiccator the length of time required is so long as to lead to the substance being completely decomposed when examined. The only way in which it seemed to be possible to reach successful results, then, would be to find a way of determining the amount of the precipitate formed, and the extent of the solubility of its sulfur in carbon disulfide, without actually drying and weighing the precipitate. The steps in the method which were tried were as follows: A solution of tellurium was first prepared, and careful determinations were made to show its tellurium content. Then known volumes of this solution were precipitated by hydrogen sulfide, and the precipitates were collected, dried and weighed, thus determining the composition of the precipitate by synthesis, since the amount of tellurium is already known by the amount of the solution taken. After repeated experiments had been made to show the exact weight of the precipitate which a given volume of the solution would give when precipitated by hydrogen sulfide, experiments similar in nature were tried, but the precipitates formed were shaken up with carbon disulfide before being collected and weighed. In this way the solubility of the sulfur in the mixture could be determined. Finally these experiments were repeated at various temperatures, and thus the question as to whether a combination between the sulfur and tellurium existed at low temperatures but not at high was determined.

I will now give the results of some determinations carried out in the manner stated and will show the results achieved:

In the first series of tests the solution of tellurium was prepared by dissolving pure tellurium in hydrochloric acid to which a few drops of nitric acid had been added (tellurium not being soluble in hydrochloric acid alone), and the solution was then heated for several hours on a sand-bath, hydrochloric acid being added from time to time until the nitric acid had been removed. The strong hydrochloric acid solution containing tellurium tetrachloride was then diluted with water and was ready for the determination of its strength. In each determination 3 cc. of the solution were taken, and enough hydrochloric acid was added so that tellurium dioxide would not be precipitated upon dilution with water. The solution was then considerably diluted and a freshly prepared solu-

tion of sulfur dioxide was added, the precipitation taking place at a temperature of 80° .

The results of four consecutive determinations of the strength of the solution gave figures as follows: 0.0734, 0.0734, 0.0738 and 0.0736 g. Te.

As it has been pointed out by other workers that in the methods of precipitating tellurium by sulfur dioxide the results are likely to be high owing to the oxidation of the tellurium, the lower value 0.0734 g. was taken as the equivalent in tellurium of 3 cc. of the solution. This quantity of the solution was found very convenient to use, and was the standard amount taken in all the determinations which will be given.

A number of tests were next made to determine the weight of the precipitate which would be formed from 3 cc. of this solution, by passing hydrogen sulfide through it as long as a further precipitate resulted. Precautions were taken to have the results of these experiments strictly comparable, and 8 determinations gave results as follows: Wt. of ppt., 0.1103, 0.1098, 0.1102, 0.1079, 0.1088, 0.1100, 0.1102 and 0.1093 g.

These results will be seen to be fairly concordant when it is considered that the determinations represent a very small weight of the material, and that, from the nature of the precipitate, the weighing has to be made of material dried at 100° . The very close relation which these results bear to the theoretical quantity of the precipitate required, assuming the substance to contain tellurium and sulfur in the ratio of Te to S_2 , will be seen by reference to these figures:

Used 0.0734 g. Te, equivalent to 0.1103 g. TeS_2 ; found 0.1103, 0.1098, 0.1102, 0.1079, 0.1088, 0.1100, 0.1102, 0.1093 g.

These results thus completely confirm Becker's and Gutbier's analyses showing that the precipitate contains its sulfur and tellurium in the ratio required for the formula TeS_2 . The next determinations taken up were made to show that carbon disulfide would dissolve out the sulfur from this precipitate if the solution was warmed during or after precipitation. These determinations were necessary only to make the work more complete, and to answer any objection which might be raised in regard to whether carbon disulfide added to the solution and shaken up with it, would really dissolve out the sulfur in the material. The reason for this step will be more clearly seen at a later stage of the work. In these determinations the same amount of tellurium (3 cc.) and water (100 cc.) was used as in all the others that have been described. Precipitated by H_2S , extracted by CS_2 , 3 cc. of solution "A," after extraction, gave 0.0776 and 0.0773 g. precipitate.

The manner in which the extraction of the sulfur by carbon disulfide was effected in these experiments, and in all those to follow, will now be described. In every case the quantity of the diluted tellurous acid solu-

tion used (3 cc. sol., 100 cc. water) was put in an Erlenmeyer flask of 250 cc. capacity, and then completely precipitated by hydrogen sulfide gas, the pressure of the gas being noted, and all precautions being taken to have conditions the same in all the experiments. When the precipitation was to take place at 0° , the flask with its contents was brought to 0° by standing for at least an hour in a bath containing ice, and hydrogen sulfide was then passed while the flask remained surrounded by the water and the ice. A bottle containing carbon disulfide was also kept at 0° by a similar bath of ice and water, and the graduate used to measure the volume of carbon disulfide used was kept cool in the same manner. After the precipitation was complete, the hydrogen sulfide was still passed for several minutes, twenty minutes in all being the usual period. Then 20 cc. of carbon disulfide were added to the flask and the whole well shaken. Under these conditions it was found that all of the precipitate was collected in the carbon disulfide, which settled to the bottom, and the precipitate and its solvent were then in intimate contact, and the flask was allowed to stand thus for fifteen minutes, all of that time being kept, of course, in a bath at 0° . The liquid was then filtered, and it was found by experiment that the presence of the two immiscible liquids together did not cause any difficulty in filtration, the operation taking place in about the normal way, but usually somewhat slower than when a simple aqueous solution was filtered. In some of the earlier experiments a small drop of water was first placed on the filter, it being then wet with carbon disulfide, the idea being to have part of its surface for the filtration of the aqueous solution and the remainder to let the carbon disulfide pass through, thus avoiding their mutually repellant action. This method was not found necessary, however, in practice.

The determinations so far mentioned prepared the way for the important ones which will now be described, and which were intended to show whether or not a compound of tellurium and sulfur really exists. If, for example, it can be shown that immediately after precipitation from a solution at 0° by hydrogen sulfide the precipitate formed does not lose any of its sulfur when treated with carbon disulfide, while it does lose its sulfur if it has been warmed or allowed to stand for some time, then the existence of an early decomposed sulfide would be indicated, and the rate at which it decomposed at any given temperature could be determined by finding the relation which the total amount of the sulfur in the compound bore to the amount which could be dissolved out by the solvent after the expiration of regular intervals.

Three experiments were first made to determine the amount of sulfur that could be extracted by carbon disulfide from the precipitate immediately after its formation, and the following interesting results were obtained:

Precipitated by H_2S and extracted by CS_2 . 3 cc. of solution "A" gave 0.0908, 0.0940 and 0.0941 g. precipitate.

It is seen from this that almost exactly half of the sulfur is found under these circumstances to be dissolved from the mixture, as will be brought out more clearly from this tabulation:

Te present in 3 cc. of the solution, 0.0734 g.

Required for TeS_2 . Gram.	Required for TeS . Gram.	Wt. ppt. found. Gram.
0.1103	0.0918	0.0908
0.1103	0.0918	0.0940
0.1103	0.0918	0.0941

It will be noted that in the first analysis given the result is much lower than in the other two determinations, and this was due to that solution having stood for a few minutes after precipitation, before the carbon disulfide was added, thus giving the unstable sulfide time to partly decompose. In every case the carbon disulfide was in contact with the precipitate for exactly the same length of time, and this time was sufficient to allow all of the sulfur to be dissolved when the compound had been decomposed by heat, thus showing that the difference in the weights of precipitates collected could not be due to any partial or incomplete dissolving of free sulfur. To still further test the matter of the decomposition of the precipitate by simple standing, a series of tests were made in which the precipitates were formed and allowed to stand (always kept at 0°) for fixed periods of time before adding the carbon disulfide. In every case it was found that the longer the precipitate stood before adding the carbon disulfide, the greater was the amount of sulfur which was removed from the mixture, and that this solubility bore a definite and regular ratio to the time of standing. The following table will give the results obtained in this manner:

Precipitated by H_2S , and extracted by CS_2 , immediately. 3 cc. of solution "A" gave 0.0941 g. precipitate.

Precipitated by H_2S , and extracted by CS_2 , after 1 hour. 3 cc. of solution "A" gave 0.0916 g. precipitate.

Precipitated by H_2S , and extracted by CS_2 , after 2 hours. 3 cc. solution "A" gave 0.0863 g. precipitate.

Precipitated by H_2S , and extracted by CS_2 , after 3 hours. 3 cc. solution "A" gave 0.0812 g. precipitate.

In all these experiments the time the precipitate was in contact with the carbon disulfide was the same, fifteen minutes, and no other condition in the making up of the solution or the bringing about of the precipitation, varied in any way. The increased solubility of sulfur was a factor simply of the time which had elapsed since the precipitation of the material.

Further experiments were made to show the effect upon the solution of the sulfide, by standing four, five, and six hours, but it will be noted that nearly all of the sulfur was extracted at the end of three hours, showing that the compound had almost entirely decomposed at the end of that time, and the removal of the remaining sulfur was quite irregular and concordant results were not obtained.

To show that the regularity shown in the series of analyses was the result of some underlying law, and not of any factor due to the manner of procedure, check determinations were run. The results were entirely concordant, when the differences are considered which the variation of even the smallest fraction of a degree in temperature would cause in the course of three hours.

Precipitated by H_2S , and extracted by CS_2 , after 3 hours. 3 cc. of solution "A" gave 0.0812 g. and 0.0827 g. ppt.

The examination of the results which I have already given will bring out the following facts:

(a) That when a solution of tellurium is precipitated by hydrogen sulfide, whether the precipitation takes place in a warm solution or one at 0° , and irrespective of whether the solution is allowed to stand several hours or not, the weight of the precipitate formed will bear the constant ratio to the amount of tellurium in the solution, of 191.6 to 127.6 (1.5017 to 1.0000), showing that the precipitate consists of tellurium and sulfur in the proportion of one atom of tellurium to two atoms of sulfur.

(b) That the sulfur in the precipitate can be dissolved out of the mixture by carbon disulfide, provided the solution containing the precipitate has been warmed after precipitation, or allowed to stand for several hours.

(c) That at the moment of precipitation half of the sulfur in the precipitate is soluble in carbon disulfide, and a residue is left containing sulfur and tellurium in the ratio expressed in the formula TeS , and the sulfur in this residue is not soluble in carbon disulfide, thus indicating that it does not exist in the free state, but is held in chemical combination with the tellurium.

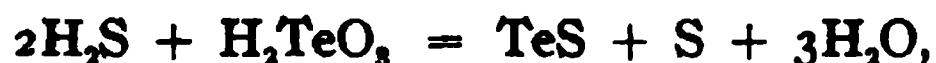
(d) That the sulfide of tellurium (TeS) present in the precipitate is very unstable, and decomposes entirely at 0° in about four hours, or instantly if heated.

Although all of the foregoing conclusions seem to me to be justifiable from the evidence which I have just stated, yet it seemed to be at least desirable to check up all these results by confirmatory experiments, and thus have the experimental data so complete that it could not be in any way questioned. I accordingly prepared a new solution differing considerably in strength from solution "A" and confirmed by additional experiments all of the evidence which I have already presented.

These experiments were found in every way to be completely confirma-

tory of the first series of experiments, the results of which have been already stated.

Until some other explanation can be found to show why this relation should hold, it seems necessary to conclude that a sulfide of tellurium, having the formula TeS , exists; that it is formed by passing hydrogen sulfide gas into a solution of tellurous acid, according to the reaction



and that this compound decomposes very readily at any temperature higher than 0° , and that it is unstable even at 0° , decomposing in about four hours to tellurium and sulfur.

PRECIPITATION OF THE COPPER-ARSENIC GROUP AND THE SEPARATION OF ITS DIVISIONS.

By J. I. D. HINDS.

Received April 1, 1912.

The analysis of solutions containing quinquevalent arsenic and bivalent tin is simplified and expedited by the method here outlined. The facts upon which the method is based are mostly well known, though I have added some definite information, especially as to the loss of arsenous chloride on boiling its acid solution and the solubility of copper sulfide in colorless ammonium sulfide. These facts have been confirmed by careful experiments and are as follows:

1. For the ready precipitation of quinquevalent arsenic by hydrogen sulfide a hydrochloric acid concentration above 2 N is required; for the complete precipitation of other members of the group, notably cadmium, antimony and tin, the acid concentration must be below 0.5 N ; to hold in solution the metals of succeeding groups the concentration must be above 0.125 N . These different concentrations are secured first by evaporation and then by proper dilution.

2. The quantity of arsenous ion lost on long boiling with dilute hydrochloric acid is a *function of the quantity present*, and when a solution normal in HCl is boiled half way, the loss is *less than one thousandth of the quantity present*. I have established this fact by many determinations, an account of which will be given in a subsequent paper. The investigation covered solutions varying in concentration from 0.01 N to normal in arsenous ion. The solutions were distilled half way and the quantity of arsenic in the distillate determined.

3. The sulfides of arsenic, antimony and stannic tin are easily soluble in colorless ammonium sulfide. Stannous sulfide is not thus soluble and its presence is avoided.

4. Copper sulfide is only slightly soluble in colorless ammonium sulfide and in this method the quantity dissolved is inconsiderable, though a

little polysulfide may be formed because of separation of sulfur or action of ferric ion.

The process is carried out as follows: To a given quantity of the solution (say 45 cc.) add one-ninth of its volume (5 cc.) of concentrated hydrochloric acid and a few drops (0.5 cc.) of nitric acid. The laboratory hydrochloric acid is usually about 10 *N* and the solution is thus made about normal. If much acid is already present allowance must be made for it. Transfer the mixture to an Erlenmeyer flask and boil it half away under the hood. The residual liquid is about 2 *N* in HCl since but little acid is lost on boiling at this concentration. The nitric acid has oxidized stannous to stannic ion, has prevented separation of metals by reduction, and has probably raised the valence of a portion of the arsenic. Pass a rapid stream of hydrogen sulfide through the hot liquid, heating again to boiling once or twice and shaking vigorously. The precipitation of arsenic begins quite promptly and proceeds rapidly. When no more precipitate forms (5 to 10 minutes), add enough water (80 cc.) to make the volume a little more than twice the original (100 cc.). This reduces the HCl concentration below 0.5 *N*. Continue to pass the gas until the liquid is cold and until no more precipitate falls (10 to 15 minutes), filter and wash. For a somewhat similar process, except as to the boiling, see Noyes and Bray.¹

Transfer the precipitate to a beaker, cover it with concentrated ammonium hydroxide, pass a rapid stream of hydrogen sulfide for one or two minutes, warm gently, shake well, filter and wash. The sulfides of arsenic, antimony and tin dissolve very promptly, carrying with them generally only a trace of copper. Filtrate and residue are treated in the usual way.

The advantages of this method are as follows: (1) A definite acid concentration is secured; (2) the precipitation of arsenic is certain, prompt and complete in a few minutes; (3) after dilution the other metals are thrown down with similar ease and certainty; (4) the use of yellow ammonium sulfide is avoided; (5) the time is much shortened, 30 to 45 minutes being sufficient for the whole process.

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THE QUANTITATIVE DETERMINATION OF PERCHLORATES.²

BY ARTHUR B. LAMB AND JOHN W. MARDEN.

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In the course of a study of certain cobaltammines it became necessary

¹ THIS JOURNAL, 29, 167, Proc. 21.

² Read before the Section of Inorganic and Physical Chemistry of the American Chemical Society at the Washington Meeting, December 28, 1911.

to make accurate analyses of perchlorates. A study of the literature indicated that no really satisfactory method of analysis had been worked out, and a number of trials by several methods confirmed this conclusion. We finally located the disturbing factor in the simplest of these methods, and by a proper mode of procedure eliminated it altogether, so that now we can determine perchlorates with ease, speed and accuracy.

A fusion method for the analysis of perchlorates, followed by the determination of the chloride formed, would seem to present no special difficulties. As a matter of fact, in spite of many attempts, it appears that no accurate results have heretofore been obtained in this way. Many different fusion mixtures and different methods of procedure have been suggested. The method of Bangley,¹ according to which the perchlorate is ignited with ammonium chloride, has been recommended, but it is admitted that an accuracy greater than 1% cannot be expected. A method described by Carnot² has also been recommended.³ In this method the perchlorate is mixed with sand in a platinum crucible and this is heated to a dull red color. Carnot claimed an accuracy of 0.1%, but in spite of repeated trials we have been unable to approach this accuracy. The results of our last two trials, made with a pure sample of potassium perchlorate, were the best, and are given in Table I:

TABLE I.—ANALYSIS OF POTASSIUM PERCHLORATE BY CARNOT'S METHOD.

No. of. expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.
1	0.4562	0.4720	0.0000	0.4593	—0.0127	—2.69
2	0.4677	0.4805	0.0000	0.4771	—0.0034	—0.70

It will be seen that the errors are very considerable. It appeared in earlier trials as though these errors might be due to a loss by volatilization, and the temperature was therefore kept as low as possible; but this could not be carried too far as there was, on the other hand, the danger of incomplete decomposition due to too low a temperature. There is no sure way by this method of avoiding these alternative difficulties.

Dupré⁴ apparently appreciated these difficulties, for in determining the perchlorates in saltpeter by ignition, he used a platinum crucible surrounded by a specially constructed oven which maintained a constant temperature of 545°. His results appear to be somewhat better than those we have obtained by the Carnot method. The results of the only analyses he publishes, where adequate amounts of perchlorate were used, are given in the following table (Table II):

¹ Treadwell and Hall, "Analytical Chem.," Vol. II.

² *Compt. rend.*, 122, 452 (1896).

³ Sutton, "Volumetric Analysis," p. 175 (1904).

⁴ *J. Soc. Chem. Ind.*, 21, 825 (1902).

TABLE II.—ANALYSES OF POTASSIUM PERCHLORATE BY DUPRÉ'S METHOD.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.
1	0.0035	0.995	0.0000	0.986	—0.009	— 1.0
2	0.0035	0.498	0.0000	0.492	—0.006	— 1.2
3	0.0035	0.249	0.0000	0.250	+0.001	+ 0.4
4	0.0035	0.099	0.0000	0.099	±0.000	+ 0.0
5	0.0035	0.050	0.0000	0.054	+0.004	+ 8.0
6	0.0035	0.025	0.0000	0.028	+0.003	+12.0

These results are still very unsatisfactory.

A method proposed by Dietrich and Ballenbach¹ appears to be the most successful modification, so far, of the fusion method. These authors fused the perchlorate with a mixture of potassium nitrate and nitrite. The only results they have published are reproduced in Table III:

TABLE III.—ANALYSES OF POTASSIUM PERCHLORATE BY DIETRICH AND BALLENBACH.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.	Flux added.
1	0.3924	0.4062	0.0000	0.4070	+0.0008	+0.19	KNO ₃ and KNO ₂
2	0.4436	0.4589	0.0000	0.4574	—0.0015	—0.32	KNO ₃ and KNO ₂

While better than any of the previously cited results their errors are still considerable.

Influenced by the ill success of these various modifications of the fusion method a number of investigators² have worked out methods of reduction and analysis in solution. One by Rothmund,³ using titanium sulfate, appears to be the most successful of them, but while apparently accurate enough, it is long and time consuming when compared with the direct fusion method. It seemed to us worth while, therefore, to locate the source of error in the fusion method and to remove it if possible.

The sign of the errors in all the modifications of this method so far tried has been almost always negative; that is, too little silver chloride has been obtained. Such a result would be caused by either of the two alternatives above mentioned, that is, either by incomplete reduction or by volatilization.

To obtain evidence bearing upon these alternatives we fused samples of pure potassium perchlorate with many different fluxes; with potassium bisulfate and zinc, with sodium carbonate alone, and with sodium carbonate mixed with sodium sulfite or powdered charcoal, or with powdered charcoal and titanium sulfate. It is not necessary to give the results of these fusions in detail. Low results were again obtained in every case, but the error was fairly constant and never amounted to

¹ *Ber.*, 38, 751 (1905).

² Rothmund, *Chem. Ztg.*, 33, 1245 (1909). Sjollem, *Z. anorg. Chem.*, 42, 127 (1904). Kreiden, *Z. anorg. Chem.*, 10, 277 (1895).

³ *Loc. cit.*

more than 1.0%, even where no reducing agent was present. The fusions with the flux containing sodium carbonate, carbon and titanium sulfate gave the best results, but even they were always from 0.2–0.4% low. The use of a double crucible with a double cover seemed to be only a slight improvement. These experiments indicated that the reducing agent was of little importance and that the small discrepancies were probably due not to incomplete reduction but to a slight loss by volatilization.

To test this conclusion a number of fusions were carried on in a glass combustion tube through which a slow current of air was drawn. Plugs of asbestos wool were inserted near the outlet end of the tube, and to this two U-tubes containing beads wet with water were attached in series. The perchlorate with flux was placed in a platinum boat and heated for about twenty minutes. The plugs of asbestos and the moistened beads prevented the escape of any chloride vapor or fumes, for, although the water in the first U tube usually gave a slight test for chlorides after a fusion, no chloride was ever detected in the second U tube. After cooling, the contents of the combustion tube and the U tube were washed upon a platinum gooch filter with hot water, the chloride precipitated, and the silver chloride dried in an electric oven at 170°–180°. Different fusion mixtures were employed; first sodium carbonate mixed with powdered charcoal and titanium sulfate; later the titanium sulfate and then the charcoal too were omitted. Since the charcoal, titanium sulfate and asbestos were all found to contain traces of chlorides, blank determinations were made upon each of them and appropriate corrections, always very small, were applied. The use of warm water in washing resulted in a rapid removal of the silver and potassium nitrate from the precipitate, but according to the measurements of Böttger¹ and Kohlrausch² must have entailed a slight loss of silver chloride. The temperature of the wash water was about 60° and its total volume, since it was applied in small quantities at a time, amounted only to between 50–75 cc. A saturated solution of silver chloride in pure water of this volume and temperature would have contained about 0.4 mg. of silver chloride, but since the washing was soon discontinued after the wash waters showed no test for silver ions, the first two-thirds of the wash water could have contained only a negligible quantity of silver chloride. The loss of silver chloride then must have been only about 0.1 mg. We have added this almost negligible correction to the observed weights of silver chloride. The results of these experiments are given in Table IV.

These results, with an average deviation from theory of only 0.2 mg. of silver chloride or 0.1%, demonstrate that accurate results can be obtained by the fusion method; that reducing agents are unnecessary and

¹ *Z. physik. Chem.*, 46, 603 (1903).

² Kohlrausch and Holborn, "Leitvermögen," p. 216.

that the low results of previous analyses by the fusion method must have been due to losses by volatilization.

TABLE IV.—FUSION ANALYSES OF POTASSIUM PERCHLORATE IN A TUBE.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.	Flux added.
3	0.2049	0.2119	0.0015	0.2134	±0.0000	±0.00	Na ₂ CO ₃ , Ti(SO ₄) ₂ , and C
4	0.2005	0.2074	0.0015	0.2086	—0.0003	—0.15	"
5	0.2506	0.2592	0.0015	0.2603	—0.0004	—0.15	"
6	0.2605	0.2695	0.0010	0.2699	—0.0006	—0.22	Na ₂ CO ₃ and C
7	0.2017	0.2086	0.0002	0.2085	—0.0003	—0.15	Na ₂ CO ₃

With these points established we resorted to a much simpler and yet equally efficient form of apparatus. It consisted merely of a thin glass (Jena) test tube of 25–30 cc. capacity fitted with two plugs of asbestos wool. The plugs were 15 mm. thick; the first was placed 50 mm., the second 95 mm. from the bottom of the test tube. The perchlorate was weighed directly into the test tube, the plugs inserted, the tube clamped in a nearly horizontal position and the lower end gently heated. White fumes were formed as the oxygen was expelled but these were completely retained by the first plug. When effervescence had ceased, a somewhat larger flame was applied until all the chloride was thoroughly fused. The time required for this heating varies between 10 and 15 minutes. It is a decided advantage to be able to watch the progress of the fusion. After cooling, the contents of the tube were washed upon a filter with warm water, the chloride was precipitated and the silver chloride dried as before. The weights were carefully calibrated and vacuum corrections applied, taking 2.52 and 5.57 as the specific gravities of the potassium perchlorate and the silver chloride, respectively. As before, a correction of 0.1 mg. was applied for the silver chloride dissolved by the warm wash water.

The same sample of potassium perchlorate which was used in the combustion tube fusions was first analyzed by this method. This sample had been found to be free from chlorides, chlorates or sulfates and from other metals than potassium. The results of these analyses are given in Table V:

TABLE V.—ANALYSES OF SAMPLE NO. 1 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
8	0.2290	0.2369	+0.0002	0.2371	±0.0000	±0.00
9	0.3455	0.3574	+0.0002	0.3577	+0.0001	+0.03
10	0.5904	0.6107	+0.0002	0.6107	—0.0002	—0.03

The average deviation from the calculated value in the analysis is but 0.02%.

A second sample of potassium perchlorate was prepared from the above

sample by a double recrystallization from redistilled water in Jena glass flasks, using as low temperatures as possible. The resulting 50 gms. of salt was ground and then dried to constant weight at 130° in an electric oven. Analyses made upon it are given in Table VI:

TABLE VI.—ANALYSES OF SAMPLE NO. 2 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
11	0.4561	0.4718	+0.0002	0.4720	±0.0000	±0.00
12	0.4437	0.4590	+0.0002	0.4590	—0.0002	—0.04
13	0.4501	0.4656	+0.0002	0.4658	±0.0000	±0.00

These results are practically identical with those obtained with the previous sample and demonstrate the purity of both.

This method was now employed to analyze a newly prepared aquopentammine cobalt perchlorate. It was necessary to dilute the cobalt-ammine, else a rather explosive decomposition took place; pure sodium nitrate was used for this purpose. The results are given in Table VII:

TABLE VII.—ANALYSES OF AQUOPENTAMMINE COBALT PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	KClO ₄ . Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
14	0.2900	0.2704	+0.0002	0.2706	±0.0000	±0.00
15	0.3342	0.3121	+0.0002	0.3124	+0.0001	+0.03

They agree nearly as well with the requirements of theory as do the analyses of potassium perchlorate.

The above analyses demonstrate beyond question the accuracy of this method. The average duration from the calculated weight of silver chloride was less than 0.02%, which is certainly equal to the attainable accuracy of the chloride determination itself under these conditions. Moreover, *every* analysis made by this new process has been here recorded. The apparatus is very simple; a hard glass test tube is preferable to an ordinary soft one, but the treatment is not severe. We used the same thin glass test tube for the first three analyses without any perceptible injury to it. The fusion can be easily controlled and the whole analysis requires scarcely more time than an ordinary chloride determination. If this latter determination is made volumetrically, the whole analysis becomes a very rapid one.

In conclusion, then, we can present the above as a very accurate, simple and rapid method for the determination of perchlorates.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL,
NEW YORK CITY.]

IODOMETRIC COPPER TITRATIONS.

BY K. SUGIURA AND P. A. KOBER.

Received April 8, 1947.

Introduction.

In studying a large number of copper salts of amino acids,¹ we obtained the copper as a hydroxide or oxide by precipitating with alkali under suitable conditions. After washing the precipitate on the filter paper and the flask thoroughly, we transferred the paper with precipitate back into the flask and dissolved with 20–25 cc. of 10% acetic acid. The resulting copper acetate was then titrated with potassium iodide and sodium thiosulfate solution in the usual manner, using starch solution, finally, as an indicator. It was noticed that these solutions *did not show a return* of the usual *blue color* of *starch* produced in these reactions, or, in other words, showed a *stable end point*; while those titrations made in the presence of nitrates gave too high results and showed an *unstable end point*.

Recently Kendall² described a technic designed to remove the nitrites, based on the use of phenol under certain conditions. According to Kendall, his method is quick and when suitably controlled gives satisfactory and accurate values. In a later article Kendall³ points out a source of error. We hope to show that the precipitation with alkali and solution with acetic acid will accomplish the same end, is simple, and accurate, removing all unnecessary and interfering substances from the copper solution.

Experimental.

As a standard solution, we employed a 0.04 *M* copper nitrate solution, made from cupric oxide,⁴ standardized many times by the electrolytic method.

The standardized 0.04 *M* copper nitrate solution is made by dissolving 3.184 g. of copper oxide in dilute nitric acid. After evaporating almost to dryness, to remove the excess of nitric acid, the copper nitrate solution was diluted and made up to one liter. To standardize this solution, we took 50 cc.⁵ of 0.04 *M* copper nitrate solution at 18°, in a platinum dish,⁶ added 2 cc. of concentrated nitric acid, 3 cc. of 95% alcohol and brought the volume with water within 1/4 inch of the edge of the platinum dish. Electric current of 0.8–1.2 amperes was then passed through the solution for about 6 hours. The end of electrolysis was shown by testing a small portion of the solution with hydrogen sulphide. When the electrolysis was finished the dish was inclined and

¹ Kober (Preliminary Communication), *J. Biol. Chem.*, 10, 9 (1911).

² Kendall, *THIS JOURNAL*, 33, 1947.

³ Kendall, *Ibid.*, 34, 317.

⁴ Eimer and Amend's tested purity product.

⁵ Carefully standardized flasks, pipets, burets and weights were used in this investigation.

⁶ The platinum dish weighed about 50 g.

the nitric acid diluted and displaced by a stream of cold water from a wash bottle. The electrodes were removed and the dish was washed once more with water and the water finally removed from the platinum dish with 95% alcohol. The dish was then dried in an oven at a temperature of 70°–90° for 5 min. and in a vacuum desiccator for about two hours, after which it was weighed.

A few examples will suffice:

Solution ¹ No.	0.04 M Cu(NO ₃) ₂ taken. cc.	Copper found by electrolysis.	Equivalent in CuO.	Theoretical amt. of CuO for 0.04 M Cu(NO ₃) ₂ .	Factor.
1	50	0.1263	0.1581	0.1592	0.993
1	50	0.1263	0.1581	0.1592	0.993
1	50	0.1264	0.1582	0.1592	0.994
<hr/>					
Average, 50		0.1263	0.1581	0.1592	0.9933
2	50	0.1261	0.1578	0.1592	0.991
2	50	0.1260	0.1577	0.1592	0.990
2	50	0.1261	0.1578	0.1592	0.991
<hr/>					
Average, 50		0.1261	0.1578	0.1592	0.9906

These results show that the cupric oxide is somewhat impure. In order to actually prove this we electrolyzed, dried and weighed portions of cupric oxide, which gave the following results:

Sample No.	CuO taken. Grams.	Cu found by electrolysis. Grams.	Equivalent in CuO. Grams.	CuO found. Per cent.	Impurity Per cent.
1	0.2539	0.2000	0.2503	98.58	1.42
2	1.6095	1.2672	1.5859	98.53	1.47
3	1.6095	1.2671	1.5858	98.53	1.47
4	1.6095	1.2670	1.5857	98.52	1.48

To determine the factor of the 0.04 N sodium thiosulfate 50 cc. of standard copper nitrate solution were diluted to 100–150 cc. After adding 2–3 drops of 1% phenolphthalein indicator, 33% alkali was added drop by drop until a slight precipitate of copper hydroxide remained undissolved. The solution was then titrated with 0.2 N carbonate-free sodium hydroxide² (containing Ba(OH)₂) until a change of color was observed. The solution, after settling, was filtered through good Swedish filter paper, and the precipitate and precipitating flask washed three or four times with a little water. The precipitate with filter paper was then transferred back into the flask and the copper hydroxide dissolved in 20–25 cc. of 10%

¹ The determinations recorded in this paper were made during the course of a year, along with other work. Therefore, many different solutions were used, and obviously, the solutions have not always the same factor.

² An excess of alkali containing carbonate will of course keep some of the copper in solution as a carbonate complex, but under the conditions given above this is impossible.

acetic acid (warming the solution, if necessary). After adding 2–4 g. of potassium iodide to the cooled solution, sodium thiosulfate was added slowly until most of the iodine had disappeared. Then a little fresh starch solution and more thiosulfate solution were added until the blue starch color was discharged. The end point under these conditions was sharp and stable. As many controls showed, the filter paper had no influence on the results.

A few examples of titration¹ follow:

0.04 M Cu(NO ₃) ₂ taken. cc.	Weight of cop- per found after electrolysis. Gram.	Dissolved in HNO ₃ , precipitated with NaOH, etc., titrated with 0.04 N Na ₂ S ₂ O ₃ . cc.	Titrated di- rectly, without electrolysis (precipi- tation method). cc.
50	0.1261	48.93	...
50	0.1260	48.88	...
50	0.1261	49.03	...
50	48.99
50	49.00
50	49.00
50	48.98
50	48.90
—	—	—	—
Average, 50	0.12607	48.95	48.97

The thiosulfate solution was kept in a dark bottle, provided with a soda lime and calcium chloride tube. In a shaded place, and at room temperatures the solution changed its strength, but slowly, as the following table shows:

Dates, March	11	12	13	14	15	16	17
Factor.....	0.9972	0.9969	0.9965	0.9959	0.9953	0.9943	0.9925

Even large amounts of nitric acid, or of any other mineral acid present in copper solutions, do not interfere with the iodometric titrations if the acid is neutralized with alkali and the copper hydroxide is filtered off and redissolved with acetic acid as described above. This is shown below:

Solution No.	0.04 M Cu(NO ₃) ₂ taken. cc.	Added HNO ₃ (conc.). cc.	Titrated by 0.04 N Na ₂ S ₂ O ₃ . cc.
I	25	0.0	25.00
I	25	0.5	25.00
I	25	1.0	25.00
I	25	2.0	24.99
I	25	3.0	24.97
I	25	4.0	25.02
I	25	5.0	25.00
—	—	—	—
Average, 25			24.997

¹ Blank tests on the reagents were made from time to time, and corrections applied when necessary.

Solution No.	0.04 M $\text{Cu}(\text{NO}_3)_2$ taken. Factor 0.991. cc.	Acid added.	Titrated by 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$ F. = 1.008. cc.
2	25	none	24.58
2	25	none	24.58
2	25	10 cc. HNO_3	24.56
2	25	10 cc. HNO_3	24.58
2	25	10 cc. HCl	24.57
2	25	10 cc. HCl	24.58
Average, 25 cc. = 24.77, 0.04 M			24.578 = 24.77, 0.04 N

The results show clearly that the amount and nature of the acid had no influence on the determination, when the copper was carefully removed as a hydroxide. That the flocculent hydrate or hydrogel may absorb a small amount of nitrate is very probable; but that the error of such an amount is small, and entirely negligible, is apparent from the results just given. The stability¹ of the end-point indicates the same conclusion.

In order to see if copper in the form of copper sulfide could be treated in the same manner and with the same accuracy, the following experiments were made:

To 25 cc. of 0.04 M copper nitrate solution neutralized with alkali in a 250 cc. beaker, 2 cc. concentrated nitric acid were added and diluted to 50–100 cc. with water. After heating to 90°–95° hydrogen sulfide was passed slowly through the solution until the precipitation was complete. The solution was then filtered through a Gooch crucible, using a very fine asbestos mat.² To insure complete precipitation the filtrate was again treated with hydrogen sulfide, and filtered if necessary. After washing the precipitate and beaker several times with a little water, the Gooch crucible³ with the copper sulfide was placed back in the same beaker and dissolved with strong nitric acid or aqua regia. This was accomplished by placing the beaker on the steam bath for 2–3 hours. After filtering off the sulfur and asbestos carefully the copper was precipitated as described above and titrated:

0.04 M $\text{Cu}(\text{NO}_3)_2$ taken. cc.	Titration from CuS with 0.04 N $\text{Na}_2\text{S}_2\text{O}_3$. cc.	Titration from controls. cc.
25	24.98	25.03
25	24.97	25.00
25	25.04	25.06
25	25.07	25.05
25	24.84	24.83
25	24.85	24.83
Average, 24.96		24.97

¹ The end point, if dust from the air is excluded, will remain constant for hours.

² Kober, *Am. Chem. J.*, 41, 430 (1909).

³ Filter paper cannot be used, instead of asbestos, as its hydrolytic products with mineral acids prevent the precipitation of copper hydroxide on neutralization.

Considering the number of manipulations and the error of buret reading, etc., the results can be considered satisfactory.

Addendum.

Just before sending this paper for publication we read the article by Peters, in the April number of THIS JOURNAL, on the same subject. The difficulties caused by varying amounts of salts, of acids, of water, of nitrates and nitrites, etc., are removed by this precipitation method. We, therefore, expect that this method will, in all copper determinations, reduce the thiosulfate titrations to a uniform basis. The study of the influence of acids, salts, volume, etc., such as is made by previous investigators, is in our scheme superfluous.

March 30, 1912.

NOTES.

On the Detection of Potassium as Cobaltinitrite.—In the last October number of THIS JOURNAL, 33, 1566, Leon T. Bowser gives a new investigation of the potassium-sodium cobaltinitrite as an excellent means for the detection of very small amounts of potassium. Though the exactness of the author's statements hardly needs any confirmation, I will state, notwithstanding, that from my own many years' laboratory practice the precipitation of potassium by the de Koninck reagent is an excellent one and by far preferable to any other method. Only in one point I cannot agree with the author. The author says: "This salt . . . has been known for fully half a century, but it is only in the last four years that its possibilities for determination of potassium have been revealed to the analytical chemist. For qualitative purposes it had enjoyed some degree of usefulness, but that it possessed some unusually valuable characteristics seemed to have previously escaped attention."

In fact L. L. de Koninck¹ employed the reaction in mention for detection of potassium in the year 1881 and since this time I myself have introduced this method in the laboratory under my management and in the guides I have written for laboratory use. In other laboratories, indeed, the reagent of de Koninck seems not to be employed in such a degree as it deserves.

H. SALKOWSKI.

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Note on the Qualitative Detection of Alkali Bicarbonates.—In preparing sodium carbonate from sodium bicarbonate for the standardization of acids, it is desirable to have a means of ascertaining whether the bicarbonate is completely decomposed or not. As there appears to be no satisfactory test for bicarbonates in the presence of large quantities of normal carbonates given in the literature, the following was devised:

¹ Z. anal. Chem., 20, 390 (1881).

The test depends first on the fact that alkali bicarbonates, on the addition of calcium chloride, precipitate CaCO_3 , with the liberation of carbon dioxide, and second, that CaCO_3 dissolves somewhat in water containing carbon dioxide with the formation of calcium acid carbonate. If the calcium acid carbonate thus formed is neutralized with ammonium hydroxide, the CaCO_3 is of course reprecipitated.

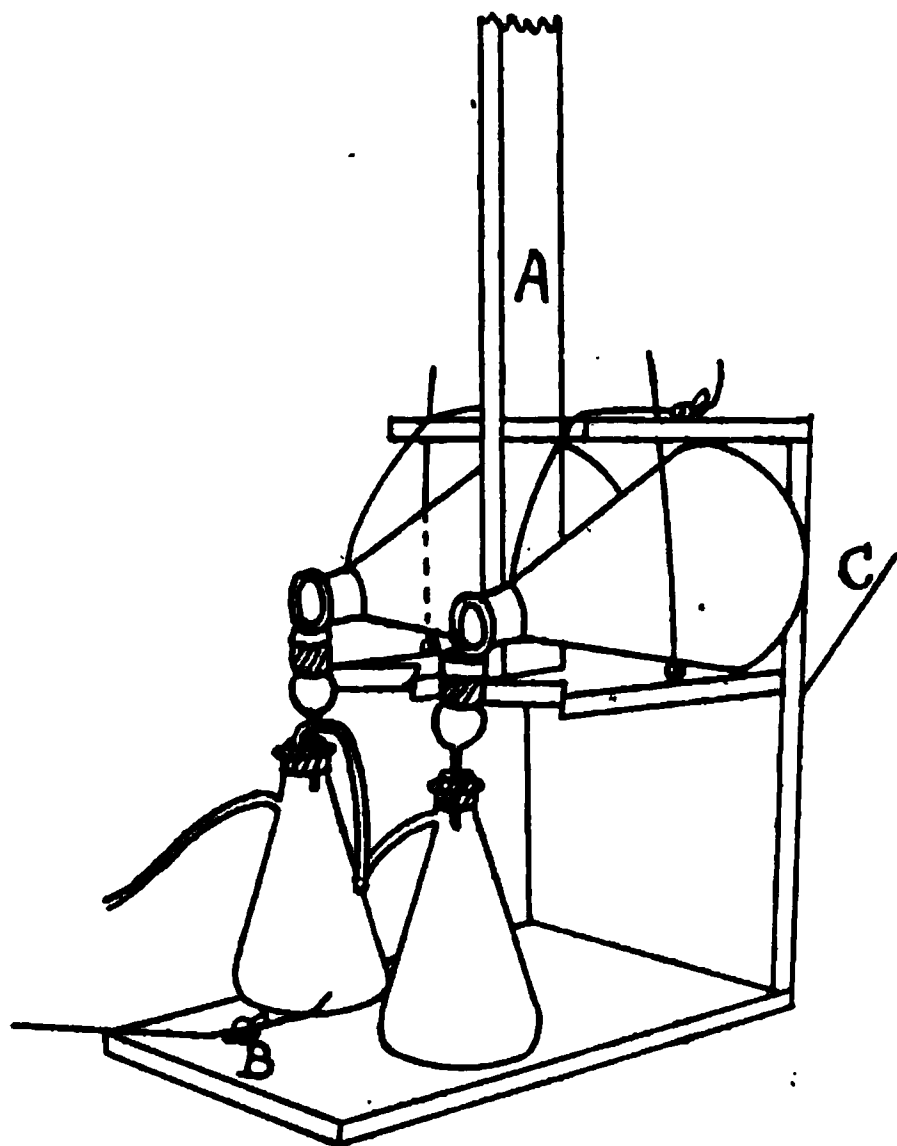
Dissolve the substance to be tested in water, that has been previously boiled to expel the carbon dioxide, and add CaCl_2 in excess. Allow this to stand four or five minutes and filter off the CaCO_3 . Then add a few drops of NH_4OH , and if the substance contained a bicarbonate, a precipitate of CaCO_3 is again obtained. With a large amount of bicarbonate the precipitation will take place in about one-half a minute, while with a very small amount the time required may be eight to ten minutes. However, with no bicarbonate a perfect blank is obtained even after long standing.

This test will detect 0.1% of NaHCO_3 in a normal sodium carbonate. The presence of ammonium salts vitiates the results on account of the solubility of CaCO_3 in such solutions.

R. T. HASLAM.

An Automatic Filter.—The apparatus as shown in the accompanying cut has been constructed by the writer in the Harvard Laboratory. It has been found to operate very satisfactorily in the filtration of the silver haloids through a Munroe-Gooch crucible.

The apparatus consists of a wooden framework to hold the bottles, which is suspended by a rigid arm (A) three feet long from a horizontal beam by a bolt in such a way as to allow the apparatus to swing with freedom. The suction flasks are held in position by straps to the bottom boards. The precipitation flasks are suspended by wires at the necks so that the lips of the flask sit well into the crucibles, and are kept in position at the sides by stout brass rods. The rods are so arranged that they easily unhook and are loose enough to admit of easy rotation of the precipitation flasks. The framework containing the bottles is held in position at either end by strong flexible wire, one piece (C) leading over



a pulley to a heavy weight, the other from the front (B) over a pulley to a drum which is attached to the works of a clock, the length of whose pendulum bob is easily adjusted to give a large variation of speed of drum. Clamps of the window sash style have at each point of attachment been used to hold the ends of the wires.

In operation the framework is first swung to the side nearest the clock so that the precipitation flasks are held in an upright position and a slight adjustment of the wire at B will start the liquid filtering. If the clock be then started and the pendulum regulated, the apparatus may be safely left, the final position of the flask being such as to drain it completely.

To wash the precipitate, the apparatus is swung to the middle position and the wash water added, the flask shaken and the liquid filtered off in the same manner as already described.

To transfer the precipitates, the crucibles and mouths of the precipitation flasks are lowered, the framework is hooked back so that the flasks incline sharply to the crucible. The precipitate may be then washed out easily and completely.

The apparatus is believed to have the following advantages: (1) less dust would fall into the analyses; (2) an especially tiresome delay of time avoided; (3) less possibility of the spilling or the overflowing of the crucible while filtering; and (4) two or more filtrations may be conducted simultaneously.

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THE OIL OF THE SOUTHERN CYPRESS.¹

BY ALLAN F. ODELL.

Received March 20, 1912.

The cones of the southern cypress (*Taxodium distichum*, Rich.) contain considerable quantities of a volatil oil, to which the odor of the cypress is in part due. It is in the fall, when these cones are maturing, that the aroma of the tree is most prominent in the swamps.

The work upon the oil from the cones was undertaken with the view of obtaining in larger quantities the peculiar aldehyde compound which was found in the resin from the wood.²

The difficulties attendant upon the distillation of the resin, which was obtained by extraction, were so numerous that this method of getting the aldehyde was discarded as unprofitable. The yield, also, was so small that definit assurance of its purity could not be had.

The cones were gathered at various periods from September to December, and each lot distilled by steam separately. The cones collected

¹ Read before the New Orleans Section, March 15, 1912.

² THIS JOURNAL, 33, 755.

in September yielded about 1% of a yellowish green oil, smelling strongly of pinene. Those collected later in the year yielded from 1½–2% of oil, which was of a darker color and had a marked citron-like odor.

The specific gravity of the oils varied from 0.86 for the oils first distilled to 0.850 for the oil last distilled. The rotation also varied from +18.0° for the first oil to +35.5° for the last oil (100 mm. tubes).

Saponification by alcoholic potash gave evidence of a very slight ester content. The acetyl saponification gave an average alcohol content of 2.5%.

About 300 grams of the oil were fractionated, at first in a vacuum, but the refractionations were conducted under atmospheric pressure, as none of the several fractions seemed to suffer decomposition by this treatment. About 85% of the oil distilled between 155–160° at atmospheric pressure. Repeated fractionations of this portion gave a fairly pure specimen of pinene, the proof for which is based on the following: d_4^{18} 0.8616; n_D^{20} 1.4655; $[\alpha]_D^{13} = +30.8$; b. p., 156–157°; nitrosochloride, m. p. 103°.

About 5% of the oil distilled from 175–180°, and after purification by refractionation, showed properties which would identify this fraction as limonene: d_4^{18} 0.8567; n_D^{20} 1.4742; $[\alpha]_D^{20} = +98.3$ (in ether); tetrabromide, m. p. 104°; nitrosochloride, m. p. 105°.

A small fraction was obtained distilling from 210–220°. This was the alcohol fraction, as was determined by the acetyl saponification process and by the readiness with which it evolved hydrogen when added to sodium in anhydrous ether. As the fraction was small, no particular attempt was made to identify the alcohol positively. When added to Beckmann's chromic acid reagent, there was immediately precipitated a copious, brown, flocculent mass. Semmler has given this test¹ as one which may be used to differentiate between true and pseudo terpene alcohols, and the only pseudo alcohol which corresponds with this one is sabinol. The constants obtained for this fraction are: d_4^{18} 0.9430; n_D^{20} 1.4881; dextro rotatory in ethereal solution.

The portion of the oil distilling between 220–235° seemed to be a mixture of the alcohol and a ketone, so that the amount of the latter present in the oil could not be ascertained, but it was apparently present in larger quantity than the alcohol.

This ketone in glacial acetic acid solution gave a semicarbazone readily when the semicarbazine hydrochloride (in acetic acid solution) was added to it. This product showed a sharp melting point of 162–163°. A good yield of the oxime could not be obtained.

The ketone was regenerated from 3 grams of the semicarbazone by warming with dilute sulfuric acid, and the mixture extracted. The

¹ Ber., 34, 708.

residue obtained by evaporation of the solvent had the following constants: d_4^{18} 0.960; n_D^{20} 1.500, which approximates the constants found for carvone.

A sesquiterpene was found in the fraction distilling from 260–275° and seemed to be identical with the sesquiterpene found in the wood,¹ though in a state of greater purity. It gave the same color reaction with sulfuric acid in acetic acid solution, and the same amorphous yellow mass on treatment with nitric acid. The constants for this are: d_4^{18} 0.9335; n_D^{20} 1.5039; dextro rotatory. These, while differing from the constants for the sesquiterpene found in the wood, are in accordance with those for a tricyclic sesquiterpene possessing a single double bond.

There was a fraction between the pinene and the limonene fractions which gave the brown flakes with Beckmann's chromic acid reagent, indicating the presence of a pseudo terpene, but no effort was made to place this body definitely, as this investigation was commenced in order to find the aldehyde previously found in the wood, and in this, the investigation was not successful.

A preliminary examination of the oil from the cypress leaves shows this oil to differ widely from the cone oil, and the investigation of the leaf-oil will be undertaken in the near future.

Summary.

The oil from the southern cypress approximates the following composition: Dextro pinene, 85%; dextro limonene, 5%; a pseudo terpene alcohol (sabinol?), 2%; carvone, 3%; a tricyclic sesquiterpene, 3%; the remainder composed of substances boiling above 275°.

No aldehydes were found in the oil.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

FASTING STUDIES. X. A NOTE ON A GLYCOGEN-FREE LIVER.

BY P. B. HAWK.

Received March 27, 1912.

The presence of sugar in the liver was first noted by Claude Bernard,² who later demonstrated that glycogen was the source of the sugar.³ From that day to the present time the nutritional relationships of this polysaccharide have been the subject of a very large number of investigations.⁴ The result has been that the origin and function of glycogen in the animal organism are now thoroughly understood.

¹ *Loc. cit.*

² Bernard and Barreswil, *Compt. rend.*, 27, 514 (1848).

³ Bernard, *Gaz. Médicale*, March 28th, 1857.

⁴ For excellent reviews of the literature see Pflüger's "Das Glykogen," Bonn, 1905, and Cremer's review in *Ergebnisse der Physiologie*, 1, 803 (1902).

It was early noted that the glycogen store of the liver and that of most of the other organs and tissues was lowered during fasting. The heart, however, has been shown to retain its glycogen content unaltered during a period of fasting long enough to decrease the glycogen store of the muscles, for example, to 4-10% of the normal. It was concluded on the basis of early experiments that the liver of an animal could be rendered "glycogen-free" provided the animal in question were subjected to a sufficiently protracted period of inanition. Later experiments cast doubt upon this finding and at present scientific workers quite generally hold to the belief that it is impossible to render the liver "glycogen-free" by means of the fasting procedure. In this connection Pflüger¹ has shown that glycogen could be demonstrated in the liver of a dog after the animal had fasted seventy-three days. In certain recently published tests from our laboratory on postanesthetic glycosuria,² data were obtained which were interpreted as indicating the gradual depletion of the glycogen store under the influence of fasting. It was there shown that fasting dogs gave evidence of a progressively decreasing glycosuria following their anesthetization by ether at intervals during the progress of a fast.

It is believed that the glycogen store of the animal body is made up in large part from the transformation of ingested carbohydrates but that there is nevertheless an actual formation continually of small quantities of glycogen within the body of the animal. On this basis, therefore, the hypothesis, that it is impossible to cause the liver of a living animal to give a negative test for glycogen, appears logical. The study of the nutritional relationship of glycogen has been given considerable stimulus through the admirable respiration experiments made by Benedict³ and collaborators in which the actual course of the glycogen combustion was carefully followed.

In connection with one of our fasting studies, we had the opportunity of examining the liver of "Oscar," our fasting dog, an animal which holds the distinction of having fasted for periods of one hundred and seventeen⁴ and one hundred and four days,⁵ respectively. The possibility of finding no glycogen present in the liver of this animal had not suggested itself to us. We knew that the glycogen reserve would be depleted in a most pronounced manner because of the great length of the fast (104 days) and we considered that a quantitative determination of the glycogen in this liver would give us some basis for concluding as to the lower limit

¹ Pflüger, *Arch. ges. Physiol.*, 119, 119 (1907).

² Hawk, *Arch. Int. Med.*, 8, 39 (1911).

³ Benedict, Carnegie Publication No. 77.

⁴ Howe, Mattill and Hawk, *J. Biol. Chem.*, 11, 103 (1912).

⁵ Howe and Hawk reported before Am. Physiol. Soc., Baltimore, 1911; proceedings, *Am. J. Physiol.*, 1912.

for the glycogen reserve as influenced by fasting. Pflüger's method¹ for the quantitative determination of glycogen was employed. *No glycogen was present.* A portion of muscle subjected to the same method also yielded negative results.

To our mind, the unusual length of the fast is associated in a very important manner with the finding of a "glycogen-free" liver. May it not be possible that the nutritional régime of a dog hardy enough to withstand a fast of 100 days will become so altered during the closing days of such a test as to render the organs and tissues glycogen-free? The dog was also a very active animal and delighted to jump in and out of his cage,² and, therefore, inasmuch as muscular work will increase the glycogen consumption it is possible that this factor had some slight influence upon the final result. It should also be borne in mind that Oscar was a "repeated" faster. It is possible that the liver of a "repeated faster" subjected to fasts of a very prolonged nature may be rendered glycogen-free, whereas glycogen will remain present in the liver of an "initial faster" through a single protracted fast.

STUDIES ON ENZYME ACTION. II. THE HYDROLYTIC ACTION OF SOME AMINO ACIDS AND POLYPEPTIDES ON CERTAIN ESTERS.

BY K. GEORGE FALK AND J. M. NELSON.

Received April 13, 1912.

1. Introduction. 2. Experimental Method. 3. Experimental Results. 4. Discussion of Results. 5. Conclusions.

1. Introduction.

Very little is known at the present time of the chemical nature of lipase. Differences in the substances which occur in lipase preparations obtained from animal or vegetable sources greatly complicate the investigation into the identity of their active constituents. It is therefore preferable to speak with Loevenhart³ of the hydrolytic action of enzymes as a definite property without assuming that this property is limited to a single substance or group of substances, until more chemical evidence of the nature of these substances is obtained. Loevenhart, in the paper referred to, discussed in detail the question "*Are the animal enzymes concerned in the hydrolysis of various esters identical?*" and concluded tentatively that while the action of the liver and the pancreas is probably to be attributed to a different single enzyme in each of these tissues, the variations in the actions on different esters by each enzyme are due to variations in the

¹ Pflüger, *Loc. cit.*

² Howe, Mattill and Hawk, *Loc. cit.*

³ *J. Biol. Chem.*, 2, 427 (1907).

admixture of substances in the extracts. A. E. Taylor¹ considers that "the question of the identity of the animal and vegetable ferments is a vain discussion. Both animal and vegetable lipases are able to accelerate the cleavage of all the simple esters of the monatomic alcohols and of glycerin, as well as of many synthetic esters."

A number of conclusions of other workers in these fields might be quoted, but as these are to be found summarized in suitable text-books, only some of the chemical evidence of the nature of lipase will be mentioned. The activity of the castor bean lipase is destroyed by pepsin or trypsin. While the activity is not destroyed by dry heating to 100°, it is lost in aqueous solution or suspension even at 65°.² The loss of activity by heating in aqueous solution is characteristic of both animal and vegetable lipases. The asymmetric hydrolysis of esters by lipase preparations has been described a number of times.³ The acceleration of lipolytic action by various substances, more or less specific for a lipase from a definite source, may for the present at any rate, be considered to be of secondary importance even though the acceleration due to these substances, the coferments, is in some cases of unusual and unexpected magnitude.

From the chemical evidence which has been quoted and from a study of the literature of lipase action, it seems reasonable to suggest as a tentative hypothesis that the hydrolytic action of lipase is due to an optically-active substance of protein character, readily hydrolyzed in aqueous solution to form lipolytically inactive substances. The characteristic groups of protein substances are the amino and carboxyl groups, free or combined in some manner. The possible hydrolytic actions of a few of the simpler amino acids and polypeptides were therefore studied.

2. Experimental Method.

The quantity of acid produced when methyl acetate, ethyl butyrate, and olive oil were dissolved or suspended in aqueous solutions containing glycine, alanine, phenylalanine, leucine, glycylglycine, leucylglycine, glycyllucine, diglycylglycine, aspartic acid and glutamic acid at 38°, was determined. The esters were neutral or very slightly acid in reaction initially (less than 0.1 cc. of 0.1 *N* alkali was required to neutralize 1 cc. ester in the extreme cases), and corrections were introduced for the amounts of acid formed from these alone in aqueous solution. Some of the amino acids were obtained from Kahlbaum; the rest of these, as

¹ *J. Biol. Chem.*, 2, 87 (1906).

² Taylor, *Loc. cit.*

³ Dakin, *J. Physiol.*, 30, 84 (1903); 32, 199 (1905). Mayer, *Biochem. Z.*, 1, 39 (1906). Warburg, *Z. physiol. Chem.*, 48, 205 (1906). Neuberg and Rosenberg, *Biochem. Z.*, 7, 191 (1907).

well as the polypeptides, from the stock prepared at different times in the Harriman Research Laboratory.¹

Three sets of measurements were necessary for each experiment: with solutions containing amino acid or polypeptide alone and ester alone, and with the mixture containing both. The formol method for which the details and necessary precautions were given by Sørensen² was used for the estimation of the amino acids and polypeptides; namely, the addition of neutralized formaldehyde solution to mask the action of the amino group and subsequent titration with alkali. A few modifications were introduced for the present work. Sørensen recommended 0.2 *N* alkali for the titrations, but because of the small increase in acidity due to any hydrolysis of ester taking place, the strength of the solutions of sodium hydroxide used was in the neighborhood of 0.1 *N*. Sørensen also recommends titrating to a definite red color with phenolphthalein as indicator. Partly on account of the presence of ester in the solutions, most of the measurements to be described were made using the first distinct pink color as end point. As it was desired to know the amount of alkali used by the amino acid or polypeptide in the solutions alone or in the presence of alkali by titrating both sets in the same way, comparable results were obtained without considering necessarily the question of the quantitative equivalence of carboxyl groups present and sodium hydroxide used. In some cases the addition of neutralized ethyl alcohol to the solutions before titration gave a more satisfactory end point. In some experiments, the titrations were carried to the definite red color, as recommended by Sørensen. Attention will be called to the experiments in which these different methods were used in connection with the tabulated results.

The method of carrying out an experiment may be outlined briefly with glycine as example. Amounts of glycine, weighing in the neighborhood of 0.1 gram each, were placed in eight flasks, 25 cc. water added to each, and 1 cc. methyl acetate each to two of them, 1 cc. ethyl butyrate to two, and 1 cc. olive oil to two. Six blanks were made up each containing 1 cc. ester (two of each ester) and 25 cc. water. The fourteen flasks were placed in the thermostat at 38° for 24 hours and then taken out and the amount of acid present determined by the formol method as follows: Five cc. of 40% formaldehyde solution, neutralized with a sodium hydroxide solution approximately 0.1 *N* with 5 drops of a 1% phenolphthalein solution in 95% ethyl alcohol as indicator, were added to each solution containing glycine, and the acid present titrated with the sodium hydroxide, using the first distinct pink color as the end point.

¹ Thanks are due to Mr. P. A. Kober and the late Dr. A. H. Koelker for having prepared and purified these substances.

² *Biochem. Z.*, 7, 45 (1907).

From the amounts of alkali used for the glycine solutions alone, and for the ester solutions alone, the amounts used by the glycine and ester in the mixtures were calculated and the differences between these and the quantities actually used in the experiments (increased by 0.04 as explained later) show the amounts of acid formed from the esters due to the presence of glycine in aqueous solution.

In all of the experiments given in the following tables (except for two sets with aspartic and glutamic acids, in which 40 cc. of solution were used), the solutions were made up to 25 cc. with water initially, 5-15 cc. of 40% formaldehyde solution (neutralized) were used in carrying out the formol method, the quantity depending upon the weight of amino acid or polypeptide used. Phenolphthalein was used as indicator throughout.

3. Experimental Results.

The experimental results are shown in Tables I-VI. In every set of experiments with each amino acid or polypeptide, simultaneous experiments were made with amino acid or polypeptide in water, amino acid or polypeptide and ester in water, and ester in water, and the amounts of ester hydrolyzed calculated in each series. In presenting the results here however, the data have been collected so that all the experiments for each amino acid and polypeptide alone in aqueous solution are given together, and from the mean of these results the quantity of alkali required for the amino acid or polypeptide in the experiments with mixtures calculated. The separate results for the ester-water and the amino acid (polypeptide) ester-water experiments are however retained.

In Table I, the results found in titrating the amino acids and polypeptides by the formol method are given. The first column indicates the substance used, the second column the weight of substance in milligrams in each experiment, and the third column the number of cubic centimeters of sodium hydroxide solution required to give a faint but distinct pink color after the addition of the neutralized formaldehyde solution. In those experiments in which the titration was carried to a red color as described by Sørensen, the letter R is placed in the first column. Where 25 cc. of neutralized ethyl alcohol were added with the formaldehyde solution before titration (Alc.) was written in the first column. The letters preceding the amounts of alkali added refer to the normality of the sodium hydroxide solutions used in titrating: $a = 0.0909$, $b = 0.1040$, $c = 0.1100$, $d = 0.1125$, $e = 0.1139$, $f = 0.1272$. In the fourth column the quantities of 0.1 N sodium hydroxide required for 1 mg. substance as calculated from the experimental data in the second and third columns are given. These are then averaged for each amino acid and polypeptide assigning to each result a weight proportional to the weight of amino acid taken initially, and the result given as "W't'd

mean.” From the weighted mean, the average deviations of the separate values (a. d.) of each set of results was calculated, and dividing this a. d. by the square root of the number of values, the average deviation of the mean¹ (A. D.) was obtained. This shows the accuracy of the results obtained in the different titrations.

TABLE I.—DETERMINATION OF AMINO ACIDS AND POLYPEPTIDES WITH ALKALI BY THE FORMOL METHOD.

Substance.	Wt. subst. in mg.	Cc. NaOH required.	Cc. 0.1 N NaOH for 1 mg. subst.
Glycine.....	78.1	d 9.15	0.1318
	83.8	d 9.82	0.1318
	91.2	d 10.72	0.1322
R.....	99.5	e 11.47	0.1313
	99.7	b 12.66	0.1320
R.....	106.2	e 12.25	0.1314
	113.8	d 13.27	0.1312
	115.1	b 14.60	0.1319
	158.0	b 19.96	0.1314
	161.4	d 18.88	0.1316
R.....	169.1	e 19.60	0.1320
	220.7	b 27.96	0.1318
R.....	239.3	e 27.76	0.1321
		W't'd mean...	0.1317
		a. d.	0.00027
		A. D.	0.00007
Alanine.....	60.0	d 5.60	0.1050
	73.8	d 6.88	0.1049
	83.7	d 7.68	0.1032
	92.1	d 8.60	0.1050
	98.0	d 8.88	0.1019
	125.3	d 11.65	0.1046
	155.2	d 13.96	0.1012
		W't'd mean...	0.1034
		a. d.	0.00140
		A. D.	0.00053
(Alc.).....	46.7	d 4.65	0.1120
(Alc.).....	66.5	d 6.50	0.1100
(Alc.).....	91.7	d 9.38	0.1151
(Alc.).....	118.4	b 12.98	0.1140
(Alc.).....	119.8	b 12.52	0.1087
		W't'd mean...	0.1121
		a. d.	0.0027
		A. D.	0.0012
R.....	58.4	e 5.50	0.1073
R.....	62.0	e 5.92	0.1088
		W't'd mean...	0.1081
Phenylalanine (Alc.).....	41.2	b 2.46	0.0606
	56.0	d 3.08	0.0619
(Alc.).....	57.4	b 3.42	0.0620
	64.9	a 4.33	0.0606

Equal to 1.18 times the “probable error.”

TABLE I (continued).

Substance.	Wt. subst. in mg.	Cc. NaOH required.	Cc. 0.1 N NaOH for 1 mg. subst.
R.....	77.2	<i>e</i> 4.05	0.0598
	89.5	<i>d</i> 4.83	0.0607
	96.9	<i>d</i> 5.22	0.0606
	107.8	<i>b</i> 6.26	0.0604
	117.2	<i>a</i> 7.96	0.0617
	127.8	<i>d</i> 6.90	0.0607
	134.8	<i>d</i> 7.26	0.0606
	158.5	<i>d</i> 8.45	0.0600
	191.1	<i>a</i> 12.77	0.0607
		W't'd mean...	0.0607
		a. d.	0.00045
		A. D.	0.00012
Leucine.....	51.0	<i>d</i> 3.43	0.0757
	66.9	<i>d</i> 4.55	0.0765
	78.9	<i>d</i> 5.30	0.0756
	90.7	<i>b</i> 6.76	0.0775
	94.7	<i>d</i> 6.40	0.0760
	97.8	<i>d</i> 6.59	0.0758
	99.0	<i>d</i> 6.54	0.0743
	102.9	<i>b</i> 7.52	0.0760
	130.0	<i>d</i> 8.58	0.0743
	131.4	<i>b</i> 9.54	0.0755
	158.0	<i>c</i> 10.76	0.0749
		W't'd mean...	0.0755
		a. d.	0.00069
		A. D.	0.00021
Glycylglycine.....	50.4	<i>d</i> 3.34	0.0746
	54.5	<i>d</i> 3.59	0.0741
	61.3	<i>b</i> 4.30	0.0730
	89.2	<i>d</i> 5.94	0.0749
	99.9	<i>d</i> 6.65	0.0749
	131.3	<i>d</i> 8.68	0.0744
		W't'd mean...	0.0744
		a. d.	0.00048
		A. D.	0.00020
Leucylglycine.....	104.3	<i>c</i> 5.10	0.0538
	119.8	<i>f</i> 5.02	0.0533
	152.7	<i>f</i> 6.38	0.0531
	156.7	<i>c</i> 7.62	0.0535
		W't'd mean...	0.0534
		a. d.	0.00023
		A. D.	0.00011
(Alc. R).....	109.0	<i>e</i> 4.83	0.0505
(Alc. R).....	130.4	<i>e</i> 5.92	0.0517
(Alc. R).....	215.3	<i>e</i> 9.77	0.0517
		W't'd mean...	0.0514
		a. d.	0.00050
		A. D.	0.00029

TABLE I (continued).

Substance.	Wt. subst. in mg.	Cc. NaOH required.	Cc. 0.1 N NaOH for 1 mg. subst.
R.....	114.7	e 5.32	0.0528
R.....	120.7	e 5.54	0.0523
R.....	138.5	e 6.40	0.0526
		W't'd mean...	0.0526
		a. d.	0.00017
		A. D.	0.00010
Glycylleucine (Alc. R).....	51.8	e 2.40	0.0528
(Alc. R).....	79.8	e 3.62	0.0517
	87.8	c 4.22	0.0529
(Alc.).....	89.3	c 4.25	0.0524
	112.7	c 5.38	0.0525
(Alc. R).....	120.2	e 5.65	0.0535
		W't'd mean...	0.0527
		a. d.	0.00043
		A. D.	0.00018
Diglycylglycine R.....	94.5	e 4.22	0.0509
R.....	97.0	e 4.34	0.0510
R.....	117.3	e 5.36	0.0520
	124.5	c 5.73	0.0506
R.....	130.9	e 5.98	0.0520
R.....	132.8	e 6.00	0.0515
	141.5	f 5.71	0.0513
	154.0	c 7.22	0.0516
	193.2	c 9.04	0.0515
	194.9	f 7.92	0.0517
		W't'd mean...	0.0515
		a. d.	0.00035
		A. D.	0.00014
Aspartic acid.....	70.6	c 8.92	0.1390
	133.5	c 16.82	0.1386
	195.1	c 24.33	0.1372
		W't'd mean...	0.1380
R.....	125.3	e 15.89	0.1444
R.....	144.9	e 18.39	0.1446
		W't'd mean...	0.1445
Glutamic acid.....	175.2	c 20.10	0.1262
	212.7	c 24.30	0.1257
	249.4	c 28.48	0.1256
		W't'd mean...	0.1258
R.....	127.4	e 14.85	0.1328
R.....	178.3	e 21.04	0.1344
		W't'd mean...	0.1337

The results shown in detail in Table I are summarized in Table II. The first column shows the substance used; the second column the number of cc. 0.1 N sodium hydroxide solution required for 1 mg. substance as given by the weighted means of Table II and the average deviations of these means (A. D.). The third column shows the number of cc. of 0.1 N

sodium hydroxide solution which 1 mg. of the substance would require theoretically; the fourth column the amount of alkali used as percentage of the theoretical amount. In the fifth column the results found by Sørensen are given, those marked R referring to a strong red color as end point, the others to a distinct red color. The results of Table I and column 2 of Table II show that no difference is obtained in titrating to different end points and correcting these in the usual way, with glycine (agreeing with Sørensen's results), glycylleucine, and diglycylglycine. With the other substances where different end points were used or where alcohol was added, different results were obtained, constant for any one method. In using these values in the subsequent tables, therefore, it is necessary in order to calculate the amount of alkali required for the amino acid taken, to use the standard corresponding to the method used in the solution titrated. As the conditions for the experiments are the same in the blanks (in Tables I and II) and when ester was present (in Tables III-VI) no error is introduced in this procedure.

TABLE II.—SUMMARY OF RESULTS OF THE DETERMINATION OF AMINO ACIDS AND POLYPEPTIDES WITH ALKALI BY THE FORMOL METHOD.

Substance.	Cc. 0.1 N NaOH for 1 mg subst. Found.	Cc. 0.1 N NaOH for 1 mg. subst. Calc.	NaOH f'd. NaOH calc. X 100.	Sørensen.
Glycine.....	0.1317 ± 0.00007	0.1332	98.9	98.5
Alanine.....	0.1034 ± 0.00053	0.1124	92.0	93.5
(Alc.).....	0.1121 ± 0.0012	"	99.7	..
R.....	0.1081	"	96.2	98.0 R
Phenylalanine.....	0.0607 ± 0.00012	0.0606	100.2	97.5
.....	"	...	99.5 R
Leucine.....	0.0755 ± 0.00021	0.0763	99.0	95.0
.....	"	...	97.0 R
Glycylglycine.....	0.0744 ± 0.00020	0.0757	98.3	97-99
Leucylglycine.....	0.0534 ± 0.00011	0.0532	100.4	...
R.....	0.0526 ± 0.00010	"	99.0	...
(Alc. R).....	0.0514 ± 0.00029	"	96.6	...
Glycylleucine.....	0.0527 ± 0.00018	0.0532	99.1	...
Diglycylglycine.....	0.0515 ± 0.00014	0.0529	97.4	...
Aspartic acid.....	0.1380	0.1503	91.8	96.5
R.....	0.1445	"	96.1	97.5 R
Glutamic acid.....	0.1258	0.1360	92.5	99.0
R.....	0.1337	"	98.3	99.5 R

Although this work was not done with the intention of studying the formol method, the results in column 4 may be of interest in this connection. These results are obtained using the first faint but distinct pink or strong red (marked R) colors as end points. With glycine, glycylleucine, and diglycylglycine, for which the end point used exerted no apparent influence, the amount of alkali used varied from 97.4-98.9% of the calculated quantity. For the substances which showed differences

depending upon the end point, results more nearly approaching the theoretical were obtained by using a deeper red color as pointed out by Sørensen. The results for leucylglycine, glycylleucine, and diglycylglycine, which were not included in Sørensen's article, approach closely to the theoretical. For the rest, there is on the whole a satisfactory agreement between the results obtained here and those given by Sørensen.

The experimental results obtained from amino acid and polypeptide and ester in aqueous solution with the production of acid are given in Tables III, IV, and V. In these tables column 1 indicates the amino acid or polypeptide used; column 2, its weight in milligrams in the experiment; column 3, the time in hours for which the experiment was allowed to run at 38° ; column 4, the normality of the sodium hydroxide solution used in titrating as indicated by the letter (see above), and the number of cubic centimeters of this solution required in titrating by the formol method by the substance-ester solution at the end of the experiment; column 5, the amount of alkali required by the ester-water mixtures under the same conditions (practically the same results were obtained here whether neutralized formaldehyde solution was added or not); column 6, the number of cubic centimeters of alkali required for the amino acid or polypeptide calculated from the standards from Table II. Column 7 contains the amount of acid produced in each experiment in terms of the normality of the sodium hydroxide solution used in titrating from the amino acid or polypeptide and ester and is equal to the result in column 4 minus the sum of the results in columns 5 and 6, plus 0.04. The end point was produced twice in the blank experiments (columns 5 and 6) and once in the mixture (column 4), and since it was found that one drop of the alkalin solution produced the necessary color in titrating to the end point used, corresponding to 0.04 cc., this quantity must be added as indicated. In order to furnish a satisfactory basis of comparison for each series of experiments and to obtain a mean value, the results given in column 8 are calculated. These show the number of cubic centimeters of 0.1 *N* acid produced by the action of 0.1 gram of the substance on the ester in question for 24 hours. These standards of comparison were chosen as they correspond to the average values used in the separate experiments, and no great error was introduced by assuming proportionality of action under these conditions. The weighted means of these results are also given for each series, assigning to each result the weight proportional to the amount of amino acid or polypeptide used in that experiment. The average deviation of the separate values from the mean (a. d.) and the average deviation of the mean (A. D.) was calculated for each series and given in column 8.

Twenty-five cc. of water were used in each experiment and 1 cc. of ester unless stated to the contrary.

Table III contains the results obtained with methyl acetate, Table IV those obtained with ethyl butyrate, Table V those obtained with olive oil.

TABLE III.—RESULTS OBTAINED WITH METHYL ACETATE AND AMINO ACIDS AND POLYPEPTIDES.

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
Glycine.....	53.7	17	<i>d</i> 6.42	0.15	6.29	0.02	0.05
	60.7	24	<i>b</i> 7.82	0.09	7.68	0.08	0.13
	101.0 ¹	44	<i>a</i> 15.40	0.14	15.14	0.16	0.08
	119.0	18	<i>b</i> 15.12	0.12	15.08	—0.04	—0.05
R.....	121.9	23	<i>e</i> 14.23	0.26	14.10	—0.09	—0.09
	129.4	18	<i>b</i> 16.56	0.12	16.40	0.08	0.08
	134.5	17	<i>d</i> 15.95	0.15	15.75	0.09	0.10
R.....	154.6	23	<i>e</i> 18.04	0.26	17.89	—0.07	—0.05
					W't'd mean...		0.02
					a. d.		0.074
					A. D.		0.026
Alanine.....	52.1	19	<i>d</i> 5.00	0.22	4.79	0.03	0.08
R.....	55.2	19	<i>e</i> 5.37	0.11	5.24	0.06	0.16
R.....	58.9	19	<i>e</i> 5.73	0.11	5.59	0.07	0.17
	60.8	17	<i>d</i> 5.70	0.15	5.59	0	0
	92.0	17	<i>d</i> 8.60	0.15	8.46	0.03	0.05
					W't'd mean...		0.09
					a. d.		0.057
					A. D.		0.026
Phenylalanine.....	48.4	17	<i>d</i> 3.08	0.14	2.61	0.37	1.21
R.....	61.6	25	<i>e</i> 3.53	0.26	3.28	0.03	0.05
	62.3	23	<i>d</i> 3.78	0.20	3.36	0.26	0.49
	82.7	17	<i>d</i> 5.02	0.14	4.46	0.46	0.88
	99.2	23	<i>d</i> 5.80	0.20	5.35	0.29	0.34
	101.3	18	<i>d</i> 6.15	0.16	5.47	0.56	0.83
	116.0	43	<i>a</i> 11.35	0.82	7.75	2.82	1.23
	146.3	18	<i>d</i> 8.76	0.16	7.89	0.75	0.77
	234.8	43	<i>a</i> 18.05	0.82	15.68	1.59	0.34
					W't'd mean...		0.65
					a. d.		0.328
					A. D.		0.109
Leucine.....	43.2	18	<i>d</i> 3.08	0.14	2.90	0.08	0.28
	48.0	18	<i>d</i> 3.56	0.14	3.22	0.24	0.75
	59.5	20	<i>d</i> 4.08	0.20	3.99	—0.07	—0.16
	63.9	20	<i>d</i> 4.40	0.14	4.29	0.01	0.02
	64.9	20	<i>d</i> 4.35	0.20	4.36	—0.17	—0.35
R.....	82.1	24	<i>e</i> 5.45	0.26	5.44	—0.21	—0.29
	84.3	20	<i>d</i> 5.94	0.14	5.66	0.18	0.29
	116.4	22	<i>c</i> 8.05	0.22	7.99	—0.12	—0.12
R.....	127.1	24	<i>e</i> 8.36	0.26	8.43	—0.29	—0.26
	187.2	22	<i>c</i> 12.80	0.22	12.85	—0.23	—0.15

¹ One-half cc. of methyl acetate used.

TABLE III *continued*).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 <i>N</i> NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
					W't'd mean...		—0.07
					a. d.		0.254
					A. D.		0.080
Glycylglycine.....	46.2	18	<i>d</i> 3.14	0.10	3.06	0.02	0.07
	72.7	20	<i>d</i> 4.98	0.16	4.81	0.05	0.09
	80.0	18	<i>d</i> 5.56	0.10	5.29	0.21	0.39
	111.6	20	<i>d</i> 7.56	0.16	7.38	0.06	0.07
					W't'd mean...		0.16
					a. d.		0.120
					A. D.		0.060
Leucylglycine.....	100.6	25	<i>c</i> 5.00	0.22	4.88	—0.06	—0.06
R.....	115.8	19	<i>e</i> 5.45	0.11	5.35	0.03	0.04
(Alc. R).....	122.7	26	<i>e</i> 5.80	0.26	5.54	0.04	0.03
(Alc. R).....	125.5	26	<i>e</i> 5.95	0.26	5.66	0.07	0.06
R.....	138.8	19	<i>e</i> 6.42	0.11	6.41	—0.06	—0.06
R.....	171.5	19	<i>e</i> 8.07	0.11	7.92	0.08	0.07
	209.9	25	<i>c</i> 10.20	0.22	10.19	—0.19	—0.10
					W't'd mean...		—0.01
					a. d.		0.060
					A. D.		0.023
Glycylleucine R.....	80.9	20	<i>e</i> 3.73	0.24	3.74	—0.21	—0.36
R.....	90.9	20	<i>e</i> 4.20	0.24	4.21	—0.21	—0.32
	107.5	24	<i>c</i> 5.28	0.22	5.15	—0.05	—0.05
	118.2	24	<i>c</i> 5.79	0.22	5.66	—0.05	—0.05
					W't'd mean...		—0.17
					a. d.		0.143
					A. D.		0.072
Diglycylglycine R.....	119.2	20	<i>e</i> 5.33	0.11	5.39	—0.13	—0.15
	128.5	23	<i>c</i> 6.16	0.38	6.02	—0.20	—0.18
R.....	129.1	20	<i>e</i> 5.83	0.11	5.84	—0.08	—0.09
R.....	131.0	20	<i>e</i> 6.06	0.26	5.92	—0.08	—0.08
R.....	151.4	20	<i>e</i> 6.83	0.11	6.85	—0.09	—0.08
	193.2	23	<i>c</i> 9.18	0.38	9.05	—0.21	—0.13
R.....	211.9	20	<i>e</i> 9.78	0.26	9.58	—0.02	—0.01
					W't'd mean...		—0.12
					a. d.		0.044
					A. D.		0.017
Aspartic acid.....	83.8	19	<i>c</i> 14.62	0.12	10.51	4.03	6.68
	158.1	19	<i>c</i> 25.20	0.12	19.83	5.29	4.65
	20 cc. ¹	22	<i>f</i> 10.14	0.24	8.09	1.85	3.44
	40 cc. ¹	21	<i>f</i> 19.00	0.12	16.19	2.73	2.66
					W't'd mean...		4.18
					a. d.		1.23
					A. D.		0.62

¹ The amount of amino acid present in these solutions was determined by titrating a number of portions; the mean values are used in column 6.

TABLE III (continued).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
Glutamic acid R.....	151.5	22	<i>c</i> 19.84	0.18	17.78	1.92	1.58
	157.5	21	<i>c</i> 20.85	0.12	18.02	2.75	2.15
	308.3	21	<i>c</i> 38.40	0.12	35.27	3.05	1.25
	15 cc. ^{1,2}	44	<i>a</i> 18.30	0.14	14.36	3.84	1.60
	20 cc. ²	22	<i>a</i> 20.30	0.15	19.15	1.04	0.65
					W't'd mean...		1.40
					a. d.		0.40
					A. D.		0.18

TABLE IV.—RESULTS OBTAINED WITH ETHYL BUTYRATE AND AMINO ACIDS AND POLYPEPTIDES.

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
Glycine.....	59.5	24	<i>b</i> 7.78	0.12	7.54	0.16	0.28
	75.1	17	<i>d</i> 9.06	0.04	8.79	0.27	0.57
	78.8	19	<i>b</i> 10.30	0.19	9.98	0.17	0.28
	101.0 ³	44	<i>a</i> 15.28	0.09	15.14	0.09	0.04
	106.0	17	<i>d</i> 12.61	0.04	12.41	0.20	0.30
	R.....	113.0	<i>e</i> 13.24	0.08	13.07	0.13	0.14
		146.1	<i>b</i> 19.06	0.19	18.51	0.40	0.36
		146.7	<i>b</i> 19.04	0.12	18.59	0.37	0.26
	R.....	212.4	<i>e</i> 24.91	0.08	24.57	0.30	0.17
					W't'd mean...		0.25
					a. d.		0.107
					A. D.		0.036
Alanine R.....	68.5	19	<i>e</i> 6.82	0.04	6.54	0.28	0.59
	71.1	17	<i>d</i> 6.56	0.04	6.53	0.03	0.07
	R.....	82.6	<i>e</i> 8.49	0.04	7.84	0.65	1.13
		118.5	<i>d</i> 10.92	0.04	10.89	0.03	0.04
					W't'd mean...		0.42
					a. d.		0.403
					A. D.		0.202
Phenylalanine.....	46.2	23	<i>d</i> 2.48	0.10	2.49	—0.07	—0.18
	46.2	17	<i>d</i> 2.76	0.16	2.49	0.15	0.52
	R.....	54.1	<i>e</i> 2.95	0.08	2.88	0.03	0.06
		77.6	<i>d</i> 4.48	0.16	4.19	0.17	0.35
		89.5	<i>a</i> 6.25	0.35	5.98	—0.04	—0.02
		90.4	<i>d</i> 5.03	0.04	4.88	0.15	0.25
		90.7	<i>d</i> 5.08	0.04	4.89	0.19	0.31
		113.2	<i>d</i> 6.10	0.10	6.11	—0.07	—0.07
		125.0	<i>a</i> 8.76	0.35	8.35	0.10	0.04

¹ One-half cc. of methyl acetate used.² The amount of amino acid present in these solutions was determined by titrating a number of portions; the mean values are used in column 6.³ One-half cc. of ethyl butyrate used.

TABLE IV (continued).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.	
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.		
					W't'd mean...		0.13	
					a. d.		0.192	
					A. D.		0.064	
Leucine.....	38.5	18	d	2.78	0.20	2.58	0.04	0.16
	44.7	18	d	3.08	0.20	3.00	—0.16	—0.54
	48.7	20	d	3.24	0.10	3.27	—0.09	—0.25
R.....	50.1	24	e	3.99	0.08	3.32	0.63	1.43
	61.6	20	d	4.36	0.16	4.13	0.11	0.24
	65.0	22	d	4.16	0.09	4.36	—0.25	—0.47
	65.7	20	d	4.44	0.10	4.41	—0.03	—0.06
	83.0	20	d	5.90	0.16	5.57	0.21	0.34
	95.0	22	d	6.12	0.09	6.38	—0.31	—0.40
R.....	95.6	24	e	6.60	0.08	6.34	0.22	0.29
	115.9	22	c	7.94	0.12	7.96	—0.10	—0.10
	117.3	22	c	7.96	0.12	8.05	—0.17	—0.17
					W't'd mean...			0.01
					a. d.			0.373
					A. D.			0.108
Glycylglycine.....	45.7	18	d	3.18	0.14	3.02	0.06	0.20
	61.5	18	d	4.20	0.14	4.07	0.03	0.07
	87.6	20	d	5.96	0.04	5.79	0.17	0.26
	108.2	20	d	7.25	0.04	7.15	0.10	0.16
					W't'd mean...			0.13
					a. d.			0.069
					A. D.			0.034
Leucylglycine (Alc. R)....	109.3	26	e	5.08	0.08	4.93	0.11	0.11
R.....	109.7	19	e	5.24	0.04	5.07	0.17	0.22
	117.5	25	c	5.78	0.12	5.70	0	0
	144.6	25	c	7.12	0.12	7.02	0.02	0.01
R.....	161.5	19	e	7.70	0.04	7.46	0.24	0.21
R.....	194.2	19	e	9.22	0.04	8.97	0.25	0.19
(Alc. R).....	285.3	26	e	13.02	0.08	12.87	0.11	0.04
					W't'd mean...			0.11
					a. d.			0.081
					A. D.			0.031
Glycylleucine.....	88.3	24	c	4.43	0.12	4.23	0.12	0.15
R.....	116.6	20	e	5.69	0.09	5.40	0.24	0.28
R.....	121.9	20	e	5.79	0.09	5.64	0.10	0.11
	222.8	24	c	10.92	0.12	10.67	0.17	0.08
					W't'd mean...			0.14
					a. d.			0.058
					A. D.			0.029
Diglycylglycine R.....	96.9	20	e	4.68	0.04	4.38	0.30	0.42
R.....	110.5	20	e	5.12	0.04	5.00	0.12	0.15
R.....	116.1	20	e	5.51	0.04	5.25	0.26	0.31
R.....	117.8	20	e	5.65	0.08	5.33	0.28	0.33

TABLE IV (continued).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
R.....	125.5	20	<i>e</i> 6.23	0.08	5.67	0.52	0.57
	159.4	23	<i>c</i> 7.54	0.14	7.46	—0.02	—0.01
	196.5	23	<i>c</i> 9.23	0.14	9.20	—0.07	—0.04
					W't'd mean...		0.21
					a. d.		0.190
					A. D.		0.072
Aspartic acid.....	91.0	19	<i>c</i> 12.77	0.10	11.44	1.27	1.94
	97.1	19	<i>c</i> 13.31	0.10	12.18	1.07	1.53
R.....	138.9	22	<i>e</i> 18.41	0.08	17.62	0.75	0.67
R.....	146.4	22	<i>e</i> 19.34	0.08	18.57	0.73	0.62
	20 cc. ¹	22	<i>f</i> 8.66	0.08	8.09	0.53	0.99
	40 cc. ¹	21	<i>f</i> 16.79	0.09	16.19	0.55	0.54
					W't'd mean...		0.95
					a. d.		0.438
					A. D.		0.179
Glutamic acid R.....	128.4	22	<i>e</i> 15.66	0.08	15.07	0.55	0.53
R.....	178.0	22	<i>e</i> 21.22	0.08	20.89	0.29	0.20
	185.9	21	<i>c</i> 22.60	0.10	21.26	1.28	0.87
	247.9	21	<i>c</i> 29.90	0.10	28.35	1.49	0.76
	15 cc. ^{1,2}	44	<i>a</i> 15.11	0.09	14.36	0.70	0.29
	20 cc. ¹	22	<i>a</i> 19.40	0.08	19.15	0.21	0.13
					W't'd mean...		0.50
					a. d.		0.255
					A. D.		0.104

TABLE V.—RESULTS OBTAINED WITH OLIVE OIL AND AMINO ACIDS AND POLY-PEPTIDES.

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
Glycine.....	33.3	24	<i>b</i> 4.36	0.04	4.22	0.14	0.44
	65.3	19	<i>b</i> 8.36	0.04	8.27	0.09	0.18
	69.3	17	<i>d</i> 8.28	0.07	8.12	0.13	0.30
	73.0	17	<i>d</i> 8.68	0.07	8.55	0.10	0.22
	87.1	18	<i>d</i> 10.36	0.04	10.20	0.16	0.28
	101.0 ³	44	<i>a</i> 15.42	0.06	15.14	0.26	0.13
	125.5	24	<i>b</i> 16.04	0.04	15.90	0.14	0.12
	128.2	19	<i>b</i> 16.52	0.04	16.24	0.28	0.29
R.....	131.8	21	<i>e</i> 15.24	0.08	15.25	—0.05	—0.05
R.....	138.5	21	<i>e</i> 16.38	0.08	16.02	0.32	0.30
	141.1	18	<i>d</i> 16.60	0.04	16.52	0.08	0.09
R.....	176.2	23	<i>e</i> 20.69	0.07	20.39	0.27	0.18

¹ The amount of amino acid present in these solutions was determined by titrating a number of portions; the mean values are used in column 6.

² One-half cc. of ethyl butyrate used.

³ One-half cc. olive oil as emulsion used.

TABLE V (continued).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.	
			Subst. ester water.	Ester water.	Calc.	Subst.		
					for subst.	ester.		
					W't'd mean...		0.18	
					a. d.		0.098	
					A. D.		0.028	
Alanine R.....	35.8 ¹	19	<i>e</i>	3.39	0.08	3.40	—0.05	—0.20
R.....	58.7 ¹	19	<i>e</i>	5.65	0.08	5.57	0.04	0.10
	84.3	17	<i>d</i>	7.90	0.07	7.75	0.12	0.23
	120.5	17	<i>d</i>	11.20	0.07	11.08	0.09	0.12
					W't'd mean...			0.11
					a. d.			0.112
					A. D.			0.056
Phenylalanine.....	50.5 ¹	21	<i>f</i>	2.28	0.08	2.41	—0.17	—0.49
	60.9	17	<i>d</i>	3.48	0.04	3.29	0.19	0.50
	77.0	23	<i>d</i>	4.15	0.06	4.15	—0.02	—0.03
	82.8	18	<i>d</i>	4.64	0.15	4.47	0.06	0.11
	95.8	43	<i>a</i>	6.86	0.24	6.40	0.26	0.14
	97.4	18	<i>d</i>	5.44	0.15	5.26	0.07	0.11
R.....	105.6 ¹	25	<i>e</i>	5.65	0.07	5.63	—0.01	—0.01
	165.4	43	<i>a</i>	11.18	0.24	11.05	—0.05	—0.02
					W't'd mean...			0.04
					a. d.			0.174
					A. D.			0.061
Leucine.....	31.8	20	<i>d</i>	2.23	0.06	2.13	0.08	0.34
	55.8	20	<i>d</i>	3.71	0.06	3.74	—0.05	—0.12
	67.5	22	<i>d</i>	4.45	0.16	4.53	—0.20	—0.36
	70.8	22	<i>d</i>	4.90	0.16	4.75	0.03	0.05
	74.3	20	<i>d</i>	4.98	0.04	4.99	—0.01	—0.02
R.....	90.8 ¹	24	<i>e</i>	6.05	0.07	6.02	0	0
	98.5	22	<i>c</i>	6.95	0.10	6.76	0.13	0.16
	99.8	22	<i>c</i>	7.03	0.10	6.85	0.12	0.14
					W't'd mean...			0.02
					a. d.			0.155
					A. D.			0.055
Glycylglycine.....	32.7	18	<i>d</i>	2.24	0.04	2.16	0.08	0.37
	51.3	18	<i>d</i>	3.43	0.15	3.39	—0.07	—0.20
	60.4	18	<i>d</i>	4.06	0.04	3.99	0.07	0.17
	108.4	18	<i>d</i>	7.26	0.15	7.17	—0.02	—0.03
					W't'd mean...			0.04
					a. d.			0.195
					A. D.			0.097
Leucylglycine R.....	125.8 ¹	19	<i>e</i>	5.80	0.08	5.81	—0.05	—0.06
R.....	127.0	19	<i>e</i>	5.87	0.08	5.87	—0.04	—0.05
	137.3	25	<i>c</i>	6.82	0.15	6.67	0.04	0.03
(Alc. R).....	149.8 ¹	26	<i>e</i>	7.03	0.07	6.76	0.24	0.17
R.....	180.1 ¹	19	<i>e</i>	8.39	0.08	8.32	0.03	0.02
	187.0 ¹	21	<i>f</i>	8.04	0.08	7.85	0.15	0.12

¹ One-half cc. olive oil as emulsion used.

TABLE V (continued).

Substance.	Wt. subst. in mg.	Time in hrs.	Cc. NaOH required.				Cc. 0.1 N NaOH for 0.1 gm. subst. for 24 hrs.
			Subst. ester water.	Ester water.	Calc. for subst.	Subst. ester.	
(Alc. R).....	192.0 ¹	21	f 8.25	0.08	8.06	0.15	0.11
	209.6	25	c 10.32	0.15	10.18	0.03	0.02
	275.8 ¹	26	e 12.70	0.07	12.45	0.22	0.08
					W't'd mean...		0.06
					a. d.		0.064
					A. D.		0.021
Glycylleucine.....	103.3	24	c 5.12	0.10	4.95	0.11	0.12
	104.7 ¹	20	e 4.79	0.08	4.84	—0.09	—0.12
	119.9	24	c 5.96	0.10	5.74	0.16	0.15
	216.0 ¹	20	e 10.19	0.08	9.99	0.16	0.10
					W't'd mean...		0.07
					a. d.		0.084
Diglycylglycine R.....					A. D.		0.042
	55.0 ¹	20	e 2.50	0.08	2.49	—0.03	—0.08
	R..... 77.4 ¹	20	e 3.42	0.08	3.50	—0.12	—0.21
	R..... 79.8 ¹	20	e 3.65	0.08	3.61	0	0
	R..... 105.6 ¹	20	e 4.95	0.07	4.77	0.15	0.19
	R..... 133.3 ¹	20	e 6.22	0.07	6.03	0.16	0.16
	154.3	23	c 7.41	0.08	7.22	0.15	0.11
	158.8 ¹	20	f 6.45	0.08	6.43	—0.02	—0.02
	173.9 ¹	20	f 7.07	0.08	7.04	—0.01	—0.01
	183.6	23	c 8.73	0.08	8.60	0.09	0.06
					W't'd mean...		0.04
					a. d.		0.100
					A. D.		0.033
Aspartic acid.....	91.2	19	c 11.73	0.04	11.44	0.29	0.44
	132.0	19	c 16.60	0.04	16.56	0.04	0.04
	20 cc. ²	22	f 8.59	0.06	8.09	0.48	0.89
	40 cc. ²	21	f 16.63	0.08	16.19	0.41	0.40
					W't'd mean...		0.39
					a. d.		0.230
Glutamic acid R.....					A. D.		0.115
	159.6 ¹	22	e 18.54	0.08	18.73	—0.23	—0.18
	R..... 179.7 ¹	22	e 21.02	0.08	21.09	—0.11	—0.08
	217.0	21	c 25.40	0.04	24.82	0.58	0.34
	243.1	21	c 28.30	0.04	27.80	0.50	0.26
	15 cc. ^{1,2}	44	a 14.65	0.06	14.36	0.27	0.11
	20 cc. ²	22	a 19.30	0.05	19.15	0.14	0.09
					W't'd mean...		0.11
					a. d.		0.146
					A. D.		0.060

¹ One-half cc. olive oil as emulsion used.² The amount of amino acid present in these solutions was determined by titrating a number of portions; the mean values are used in column 6.

TABLE VI.—SUMMARY OF RESULTS OBTAINED WITH ESTERS AND AMINO ACIDS AND POLYPEPTIDES.

(Amounts of acid produced in equivalents $\times 10^{-4}$ in 24 hours at 38° .)

	Methyl acetate.	Ethyl butyrate.	Olive oil.
Glycine.....	0.02 ± 0.026	0.25 ± 0.036	0.18 ± 0.028
Alanine.....	0.09 ± 0.026	0.42 ± 0.202	0.11 ± 0.056
Phenylalanine.....	0.65 ± 0.109	0.13 ± 0.064	0.04 ± 0.061
Leucine.....	-0.07 ± 0.080	0.01 ± 0.108	0.02 ± 0.055
Glycylglycine.....	0.16 ± 0.060	0.13 ± 0.034	0.04 ± 0.097
Leucylglycine.....	-0.01 ± 0.023	0.11 ± 0.031	0.06 ± 0.021
Glycylleucine.....	-0.17 ± 0.072	0.14 ± 0.029	0.07 ± 0.042
Diglycylglycine.....	-0.12 ± 0.017	0.21 ± 0.072	0.04 ± 0.033
Aspartic acid.....	4.18 ± 0.62	0.95 ± 0.18	0.39 ± 0.12
Glutamic acid.....	1.40 ± 0.18	0.50 ± 0.10	0.11 ± 0.06

4. Discussion of Results.

The results given in detail in Tables III–V are summarized in Table VI in which the weighted means and average deviations of these means for each set of results are given for the equivalents $\times 10^{-4}$ of acid produced from the ester heading columns 2, 3, and 4 by 0.1 gram of the amino acid or polypeptide in the first column in 24 hours at 38° . The actions caused by 0.1 gram of substance instead of by equivalents are given since the experimental results corresponded more closely to the former.

Glycine and alanine show the greatest amount of action with ethyl butyrate and least with methyl acetate. Phenylalanine on the other hand shows a markedly greater action with methyl acetate, less with ethyl butyrate, and least with olive oil. Leucine gave practically no action with any of the three esters. Glycylglycine gave the same slight action with methyl acetate and ethyl butyrate but none with olive oil. With leucylglycine, glycylleucine, and diglycylglycine, maximum, though small, actions were obtained with ethyl butyrate, very slight but distinct with olive oil, while with glycylleucine and diglycylglycine and methyl acetate, negative values were obtained. Not enough measurements were made with the former to make this last result certain. A possible explanation for these two results may be the comparatively large correction of the ester-water blank experiments which may not be applicable directly to the polypeptide-ester-water mixture. With aspartic and glutamic acids, the order of magnitude of action is methyl acetate, ethyl butyrate, olive oil. Considerably greater action was caused by the aspartic acid than by the glutamic acid as would be expected from the greater ionization constant of the former. A comparison of these actions with the action of the mixture of glycine and acetic acid containing the same amount of carboxyl groups is of interest. From some results which will be communicated later, it was found that the hydrolytic action of this mixture corresponded very closely to that of the glutamic acid solution.

5. Conclusions.

The hydrolyses of the esters by the amino acids and polypeptides which are described in this paper are in themselves not unexpected. The interesting feature of these actions is however their selective character. With amino acids which differ from each other to such a small extent as glycine and phenylalanine, and with the similar esters methyl acetate and ethyl butyrate, glycine has the greater action on ethyl butyrate, and phenylalanine on methyl acetate. The greater action of the dipeptides on ethyl butyrate and of the dibasic amino acids on methyl acetate is also of interest. This selective action with different esters is strongly suggestive of the selective action of lipases from different sources with different esters. It seems probable that many of these selective actions of the lipases may be reproduced with amino acids and polypeptides of varying structure or in the presence of other substances.

On the other hand, there is no evidence that the hydrolytic action of lipase is to be attributed to amino acids or polypeptides. The specific groupings present in the amino acids or polypeptides which show this activity may be present in more complex substances such as the proteins, and from this point of view the study of the hydrolytic actions of the decomposition products, such as the amino acids from preparations possessing lipolytic activity, and of the more complex polypeptides or other substances synthesized from them, may throw light upon the substances capable of causing such lipolytic action. The study of the influence of various added substances upon these hydrolytic actions is a necessary accompaniment of an investigation of this nature.¹

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NEW BOOKS.

The Elements of Qualitative Chemical Analysis, with Special Consideration of the Application of the Laws of Equilibrium and of the Modern Theories of Solution. By JULIUS STRIEGLITZ, Professor of Chemistry in the University of Chicago. Two Volumes. Vol. I, Parts I and II. Fundamental Principles and their Application. pp. x + 312. Vol. II, Parts III and IV. Laboratory Manual. pp. viii + 151. New York: The Century Co. 1911. Price, I, \$1.40; II, \$1.20.

The first volume of this text on qualitative analysis represents the greatest advance in the presentation of the principles of analytical chemistry which has been made since the publication in 1894 of the first edition of Ostwald's "Wissenschaftliche Grundlagen der Analytischen Chemie."

¹ A large number of experiments were carried out in which glycine, alanine, phenylalanine, and tyrosine, in the presence and absence of acids and alkalis in solutions of known H^+ ion concentration, and also in the presence of phosphates, were dissolved with cane sugar in water and the optical rotations determined at stated intervals. No evidence was obtained in any of these experiments to show that the amino acid affected the course of the hydrolysis of the cane sugar in any way.

The revised editions of the latter book have failed to keep pace with the rapid progress of the subject, and this makes the present work doubly welcome. It is remarkable that so much important theoretical material could remain so long without expression in the form of a text, but Professor Stieglitz has now succeeded in bringing together in an elementary form practically all of the physico-chemical work which bears upon the problems which arise in the analytical study of aqueous solutions. Indeed, although elementary in its nature, there is perhaps no other book which so well presents a survey of the important fundamental problems which the workers in the field of the theory of solutions are now endeavoring to solve. That this has been done so well in an elementary text is explained by the fact that the author, *contrary to the usual practice*, believes in considering his subject as still in the making, and in presenting it in such a way as to produce a thinking, productive chemist. To this end frequent discussions are presented as to the present views of different schools of physical chemists upon disputed points, and these are often accompanied with illuminating suggestions as to the methods which will most effectively lead to a settlement of the question at issue. Throughout the text frequent references are given to the original literature.

"Finally, to arouse and develop the critical questioning attitude of the professional chemist, the subject matter of the laboratory work, given in Part III, is put largely in the form of questions, which demand not only careful observation on the part of the student but also a thoughtful interpretation of the observations made." These questions upon the preliminary experiments for the different metals and acids are so put that they force the student to gain a mastery over the theoretical part of the work.

Part I treats of such subjects as osmotic pressure, electrolytic dissociation, the electron theory of valence, chemical equilibrium, colloids, and the solubility product, and Part II deals with the application of the principles to such problems as the analytical treatment of amphoteric substances, the hydrolysis of salts, fractional precipitation, precipitation with hydrogen sulfide, the theory of complex ions, and ends with two valuable chapters on the theory of oxidation and reduction from the standpoint of potential differences. The oxidizing power of permanganic acid is, for example, represented by the value of the constant $k = \text{Mn}^{++++++}/\text{Mn}^{++}$ for the reaction $\text{Mn}^{++++++} \rightleftharpoons \text{Mn}^{++}$. The treatment of the subject is not a quantitative one, but the values of the constants are considered in order that the student may learn to judge for himself as to the direction which an oxidation-reduction reaction will take.

Part IV contains the directions for the solution and systematic analysis of inorganic substances. The methods of analysis give good results, but it is to be expected that each instructor will, in teaching, modify

this part of any text on qualitative analysis to suit his individual preferences. The choice of solvents to suit the properties of the substances to be dissolved is a good feature of the scheme, as is also the preliminary extraction of lead and silver salts from the insoluble portion.

Although much of the theoretical material in this book is far more advanced in its nature than that usually contained in texts on qualitative analysis, the theoretical and the analytical work have been so skilfully interwoven, and the presentation is so clear, that the book may be used successfully in colleges where the students begin the subject with only a good high school course as a preparation, and it is found that such students enjoy particularly the theoretical part of the text. Indeed, actual experience has proved to the writer of this review that this is the most "teachable" chemistry text he has ever used. May the day come quickly when a text of the same type will appear for the subject of physical chemistry!

It will be difficult for the Century Co. to secure other texts which will at all deserve a place in the same series with their first two chemistry publications.

WILLIAM D. HARKINS.

A Handbook of Organic Analysis, Qualitative and Quantitative. By HANS THACHER CLARKE. With an introduction by J. Norman Collie. 1911. London: Edwin Arnold. viii + 264 pp. Longmans Green & Co., New York. Price, \$1.40.

"It is by no means easy to arrange a general plan for testing organic compounds so that one can say for certain what the particular compound may be. But as organic chemistry is an eminently practical science, there ought to be good practical books dealing with the subject—books where the descriptions are concise, where the treatment of the subject is systematic and not merely an enumeration of special tests for special compounds and where the student has to use his head as well as the information supplied by the text-book. Mr. Clarke has, in this book, recognized these requirements."

The material is arranged as follows: 1. Preliminary investigations: purity, qualitative tests for the elements, tests for approximate constitution. 2. Examination for radicles. 3. Separation of mixtures of organic compounds. 4. Classified tables of common organic compounds; examination of alkaloids and dyestuffs. 5. Quantitative determination of constituent elements. 6. Quantitative determination of radicles. 7. Determination of some physical properties. Index.

The method of identification is divided into four parts: tests for the elements; tests for certain classes of compounds, depending upon the elements present; tests for various salient radicles in the molecule; determination of constants and identification through the tables. As is the case with any complex method, its value can be determined only by actual laboratory experience. The tables of organic compounds, while

not as complete as those found in Mulliken, contain all of the commoner compounds, arranged in classes according to their boiling points or melting points and for most examinations will prove satisfactory. The book is far from up-to-date in its quantitative methods, the better and shorter modern laboratory practice being omitted. Thus, we do not find the Dennstedt or the electrical methods for carbon and hydrogen, the sodium peroxide or the Stepanow methods for halogens or the sodium peroxide method for sulfur. The Dumas method for nitrogen needs revision and the later methods for molecular weight and vapor density need to be added. The work is well printed and very free from typographical errors. The book furnishes much material in a small compass and will be of assistance to any one testing organic substances.

CLARENCE J. WEST.

The Chemistry of the Radio-Elements. By FREDERICK SODDY, F.R.S., Longmans, Green and Company. pp. 92. Price, 2s. 6d.

A number of excellent books have been published dealing with radioactivity in general, but primarily from the standpoint of the physicist. The present volume will therefore be welcomed by chemists as it gives a comprehensive but succinct account of the chemistry of the radio-elements. There is probably no one better adapted to write the book than Prof. Soddy, and the result has been a volume not too technical for the average chemist and at the same time detailed enough and sufficiently up-to-date to make it indispensable to the chemist who is doing work on radioactivity. The first chapter deals with a general description of radioactivity, the second with radioactive constants and the third with the classification and nomenclature of the radio-elements. Each of these elements is then taken up and its chemistry discussed in some detail. If one were disposed to criticize what is really an excellent work it might be suggested that the first chapter, "A General Description of Radio-Activity," is not detailed enough for the chemist who has not previously given some attention to the subject and entirely superfluous to the one who has. In a second edition the list of references should be fuller.

R. B. MOORE.

